

RAMAN SPECTROSCOPIC STUDIES OF  
MANGANESE CHLORIDE-ALKALI  
METAL CHLORIDE SYSTEMS

CENTRE FOR NEWFOUNDLAND STUDIES

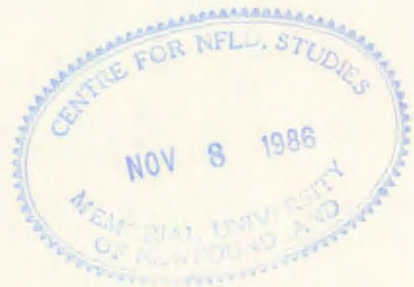
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RAMAN SPECTROSCOPIC STUDIES OF MANGANESE  
CHLORIDE-ALKALI METAL CHLORIDE SYSTEMS

by



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## Abstract

The Raman and visible spectra of  $\text{MnCl}_2 - \text{ACl}$  systems ( $\text{A} = \text{Li}, \text{Na}, \text{K}, \text{Rb}$  and  $\text{Cs}$ ) were investigated in the solid and the molten phases to identify possible species formation. The many solid compounds precipitated from the melts were identified by their characteristic spectra. The agreement with reported phase diagrams was good. The results indicated that the  $\text{MnCl}_4^{2-}$  ions were present in solid  $\text{Cs}_2\text{MnCl}_4$  and  $\text{Cs}_3\text{MnCl}_5$  but in the other compounds the manganese was octahedrally coordinated with bridged chlorides.

The Raman spectra of the solids were discussed in terms of factor group analysis. The data for the melts suggested that a discrete  $\text{MnCl}_4^{2-}$  species was the predominant species in the molten phase of composition  $\text{MnCl}_2.n\text{ACl}$  ( $n \geq 2$ ). For melts of composition  $\text{MnCl}_2.n\text{ACl}$  ( $n < 2$ ) a tetrahedral species with corner sharing was proposed but no new peaks due to new discrete species could be identified. Melts of high  $\text{MnCl}_2$  content appeared to have a very rapid equilibrium of ions with most Mn retaining tetrahedral coordination but some octahedral coordination was also suggested from assessment of visible spectra. A rapidly fluctuating local structure around the  $\text{Mn}^{2+}$  with lifetime of the aggregate on the time scale of  $10^{-12}$  seconds would be consistent with the composition and temperature studies of the bandshape of the Mn-Cl stretching region.

The Raman spectra of  $\text{MgCl}_2 - \text{CsCl}$  and  $\text{MgCl}_2 - \text{KCl}$  systems were investigated in the molten phase for comparison. The results confirm the presence of discrete  $\text{MgCl}_4^{2-}$  ions as the predominant species in melts even of low  $\text{MgCl}_2$  concentration, but a distinct polynuclear species  $\text{Mg}_2\text{Cl}_7^{3-}$  was also formed when the  $\text{MgCl}_2$  concentration was



increased. In contrast to the manganese system the equilibrium species present in the magnesium system have lifetimes greater than  $10^{-12}$  seconds. The results also indicated that by increasing the temperature the polynuclear species was broken down and more  $\text{MgCl}_4^{2-}$  ions were formed.

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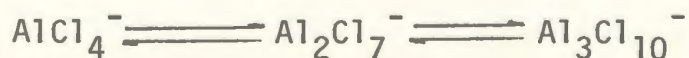


## 1. Introduction

Raman spectroscopy can be used to study, identify and characterize discrete species and ions that exist in melts and to monitor changes that accompany changes in temperature and composition. For instance the Raman study<sup>1</sup> of molten aluminium fluoride-alkali metal fluoride mixtures, indicated an equilibrium between the tetrahedral species  $\text{AlF}_4^-$  and the octahedral species  $\text{AlF}_6^{3-}$ . The spectra of mixtures of  $\text{AlF}_3$  with 53.8, 59.4, 62.5, and 75 mole % of alkali fluoride were obtained. The Raman spectrum of the melt of composition 53.8 - 46.2 mole %  $\text{AlF}_3$ -AF contain one strong polarized peak at  $623 \text{ cm}^{-1}$  and three depolarized peaks at 760, 322, and  $210 \text{ cm}^{-1}$ . These peaks were attributed to the  $\text{AlF}_4^-$  tetrahedral species. However another two peaks were detected, one polarized located at  $555 \text{ cm}^{-1}$  and the other one a weak shoulder located around  $345 \text{ cm}^{-1}$ . It was observed that the intensity of these two peaks increased at the same rate by increasing the concentration of alkali metal fluoride. These two peaks were attributed to the species  $\text{AlF}_6^{3-}$ . The spectrum of the melt of 25 mole %  $\text{AlF}_3$  contained three peaks one polarized located at  $555 \text{ cm}^{-1}$  and two depolarized peaks located at 390 and  $345 \text{ cm}^{-1}$ . These three peaks were attributed to the octahedral  $\text{AlF}_6^{3-}$  species the most likely species at this composition. The results indicated that a melt of composition close to 50-50 mole %  $\text{AlF}_3$ -AF contained almost only  $\text{AlF}_4^-$  ions, but the  $\text{AlF}_4^-$  ions were replaced by  $\text{AlF}_6^{3-}$  ions upon decreasing  $\text{AlF}_3$  concentration. For the melt of 25 mole %  $\text{AlF}_3$  no  $\text{AlF}_4^-$  could be detected spectroscopically and the melt contain almost pure  $\text{AlF}_6^{3-}$  ions. Thus the Raman study established the equilibrium between  $\text{AlF}_4^-$  and  $\text{AlF}_6^{3-}$  ions in the molten state i.e.,



Another example of the application of Raman spectroscopy to the identification and characterization of discrete species was the Raman study<sup>2</sup> of Aluminium chloride-Alkali metal chloride melts. In this case the geometry remained tetrahedral but a polynuclear species was formed. The results suggested the formation of  $\text{AlCl}_4^-$ ,  $\text{Al}_2\text{Cl}_7^-$ , and  $\text{Al}_3\text{Cl}_{10}^-$  species in the melts. Four peaks were observed for the melt of 50 mole %  $\text{AlCl}_3$ , one polarized and three depolarized and attributed to the presence of  $\text{AlCl}_4^-$  tetrahedral species. The relative intensities of these four peaks decreased by increasing  $\text{AlCl}_3$  content. When the  $\text{AlCl}_3$  concentration was increased from 50 to 66.7 mole %, new peaks were observed to increase in relative intensity. These peaks were attributed to the formation of  $\text{Al}_2\text{Cl}_7^-$  species which possibly has two distorted  $\text{AlCl}_4^-$  tetrahedra sharing one bridging  $\text{Cl}^-$ . Upon increasing the  $\text{AlCl}_3$  content from 66.7 to 75.0 mole %, four peaks were detected and increased relative to the  $\text{Al}_2\text{Cl}_7^-$  peaks. These four peaks were attributed to the formation of  $\text{Al}_3\text{Cl}_{10}^-$  species. Thus the Raman study established the existence of the equilibrium in the molten state i.e.,



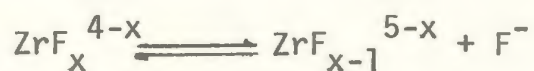
The above Raman studies gave information about the presence and the coordination of new complex species which have lifetimes greater than  $10^{-12}$  sec. which is the limit for Raman studies. In fact NMR studies of  $\text{AlCl}_4^-$  suggest that this species has a lifetime  $\sim 10^{-5}$  sec.<sup>3</sup>



The interpretation of Raman measurements are not always as straightforward. Rapid equilibrium between species and severe band overlap may preclude the identification of peaks due to discrete species.

An interesting example of a Raman study of this type was the study<sup>4</sup> of LiF-NaF-ThF<sub>4</sub> molten salt system. In this case severe band overlap prevented the separation of peaks due to specific species. This study established the coordination behaviour of Th(IV) in these melts. Two peaks were observed for the melt of 14 mole % ThF<sub>4</sub> in LiF-NaF (40-46 mole %) at 650°, one polarized band at 474 cm<sup>-1</sup> attributed to the symmetric stretching of ThF<sub>x</sub><sup>4-x</sup> species and another depolarized peak centered at 250 cm<sup>-1</sup>. It was noted that the position of the polarized peak remained unchanged for composition changes from 14 to 20 mole % ThF<sub>4</sub>, the frequency increased to 478 cm<sup>-1</sup> when the concentration of ThF<sub>4</sub> was changed from 20 to 25 mole %, and no further frequency shift was observed by increasing ThF<sub>4</sub> content more than 25 mole %. The formation of ThF<sub>8</sub><sup>4-</sup> species was proposed for melt of 14-20% mole ThF<sub>4</sub>, while for melts of 20-25% ThF<sub>4</sub> the presence of ThF<sub>7</sub><sup>3-</sup> species was suggested. Similar melts have been investigated by Raman spectroscopy<sup>5</sup>. Raman spectra of molten LiF-NaF-ZrF<sub>4</sub> mixtures at 650° have been studied to monitor the coordination of Zr(IV) in alkali metal fluoride melts. The formation of eight-, seven-, six-, and five coordinated zirconium in molten fluoride was inferred from frequency shifts upon changing ZrF<sub>4</sub> content. An equilibrium of several ZrF<sub>x</sub><sup>4-x</sup> species (where X = 8, 7, 6, and possibly 5 or 4) was proposed in molten fluorides and is dependent on the fluoride ion concentration i.e.,





No new Raman lines were observed for Th(IV) and Zr(IV) melts upon changing the concentration, but equilibrium species were suggested from frequency shifts of the polarized peak. This suggests that the lifetime of these species is  $\sim 10^{-12}$  sec. and the fluoride exchange rate is too fast to detect equilibrium species. It is also possible that the peak frequencies for the different species are similar and environmental broadening prevents band separation.

Studies of molten salts are important because of their use in electrowinning of metals from melts; for instance the production of Aluminium<sup>6</sup> by electrolysis of Alumina ( $\text{Al}_2\text{O}_3$ ) dissolved in molten cryolite ( $\text{Na}_3\text{AlF}_6$ ). Aluminium is deposited as a liquid at the cathode, it is heavier than the electrolyte so it remains at the bottom of the cell. Pure cryolite has a melting point of  $1009^\circ\text{C}$  but cryolite-alumina eutectic melts at  $962^\circ\text{C}$ . Additives (such as  $\text{LiF}$ ,  $\text{NaCl}$ , and  $\text{CaF}_2$ ) can be used to decrease the melting point, viscosity, vapour pressure and density of the melt. Also Magnesium<sup>6</sup> has been produced by electrowinning process from  $\text{MgF}_2$  melt containing  $\text{MgO}$  as an additive to lower the melting temperature of the electrolyte bath.

Knowledge of the species present in the melts is important for process improvements. In the present study  $\text{MnCl}_2$  was studied for comparison with  $\text{MgCl}_2$  since discrete polynuclear species have been observed for  $\text{MgCl}_2$  but preliminary results indicated that the  $\text{MnCl}_2$  system did not reveal new polynuclear species. This was surprising since the ionic radii of  $\text{Mg}^{2+}$  and  $\text{Mn}^{2+}$  are quite close and they have the same charge.

Phase equilibrium studies along the solid metal equilibrium line also provides information about the solids which crystallize from melts. New salts of useful properties such as  $\text{Li}_2\text{MnCl}_4$ , a solid state conductor have now been detected from Raman studies. A previous phase diagram study failed to reveal this compound.

Visible spectroscopy has also been used to characterize the coordination of the manganese salts. In an octahedral environment  $\text{Mn}^{2+}$  absorbs the  $21000\text{-}16000\text{ cm}^{-1}$  region and the samples are red however in a tetrahedral environment  $\text{Mn}^{2+}$  absorbs in the  $23000\text{-}19000\text{ cm}^{-1}$  region and the samples are yellow. In the present study the  $\text{MnCl}_2 \cdot n\text{ACl}$  samples were studied by visible absorption spectroscopy in an effort to establish the  $\text{Mn}^{2+}$  coordination in the various samples.



## 1.1 Previous Work

In addition to the related studies mentioned in the introduction there have been a number of related studies of  $\text{ACl-MCl}_2$  systems which will be reviewed below.

Early Raman measurements on molten  $\text{MgCl}_2$  and  $\text{MgCl}_2\text{-KCl}$  by Balasubrahmanyam<sup>7</sup> were interpreted in terms of  $\text{MgCl}_6^{4-}$  in pure  $\text{MgCl}_2$  and  $\text{MgCl}_3^-$  in  $\text{KMgCl}_3$  but these results were shown to be flawed by peaks due to instrumental artifacts<sup>8</sup>.

Maroni et. al.<sup>8</sup> studied Raman spectra of  $\text{MgX}_2\text{-KX}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{and I}$ ) over a range of  $\text{X}^-/\text{Mg}^{2+}$  mole ratios in the molten state. The results for  $\text{MgCl}_2\text{-KCl}$  and  $\text{MgBr}_2\text{-KBr}$  systems were interpreted in terms of discrete  $\text{MgX}_4^{2-}$  complex ion in equilibrium with a residual ionic lattice at high  $\text{MgCl}_2$  concentration, i.e., a polynuclear complex  $[\text{MgX}_2]_p$ , similar in structure to solid  $\text{MgCl}_2$  and solid  $\text{MgBr}_2$ . Polynuclear aggregates have also been proposed for  $\text{SnCl}_2\text{-KCl}$  and  $\text{ZnCl}_2\text{-AlCl}_3$  melts<sup>11,12</sup>. It was found that the concentration of  $[\text{MgX}_2]_p$  species decrease by increasing the  $\text{X}^-/\text{Mg}^{2+}$  mole ratio from 2.5 to 4.0. The Raman spectra of  $\text{MgI}_2\text{-KI}$  system of  $\text{I}^-/\text{Mg}^{2+}$  mole ratio 3.0 and 3.5 indicated the presence of a single highly symmetric species, and the observation of two depolarized peaks in the low frequency region for this species is consistent with the existence of  $\text{MgI}_4^{2-}$  of tetrahedral structure. The experimental data suggested that at  $\text{X}^-/\text{Mg}^{2+}$  mole ratio near 4.0, the  $\text{MgX}_4^{2-}$  ions of tetrahedral geometry are the predominant species in all three systems.

The Raman spectra of  $\text{MgX}_2\text{-KX}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{and I}$ ) with  $\text{X}^-/\text{Mg}^{2+}$  mole ratios near 4.0 have been studied in the molten state<sup>9</sup>. One polarized peak and three depolarized peaks were observed for each halide melt.



For  $\text{MX}_4$  molecules<sup>7</sup> of  $T_d$  symmetry, four vibrations are expected as follows:

$$\Gamma_{T_d} = \underset{\text{R}}{A_1} + \underset{\text{R}}{E} + \underset{\text{IR/R}}{2T_2} \quad (1)$$

The  $A_1$  and  $E$  modes are Raman active and the  $T_2$  modes are IR and Raman active. The Raman spectra and normal coordinate analysis calculations strongly indicated the existence of tetrahedral complexes  $\text{MgX}_4^{2-}$ .

The Raman spectra of single crystal and molten  $\text{MgCl}_2$  have been studied by Capwell<sup>10</sup>. The existence of discrete complex ions was not supported. Two peaks were observed at 243 and 157  $\text{cm}^{-1}$  in the spectrum of the crystal and assigned to the totally symmetric  $A_{1g}$  mode and the  $E_g$  mode respectively. Two peaks at 195 and 102  $\text{cm}^{-1}$  in the melt were assigned to residual lattice modes by analogy to the spectrum of the crystal. He concluded that the melt was structurally similar to the layered solid.

The IR and Raman spectra of  $(\text{NEt}_4)_2\text{MgCl}_4$  have been studied by Davies<sup>13</sup>. Four Raman peaks were observed in the solid state, one observed at 257  $\text{cm}^{-1}$  was observed as a polarized peak in acetonitrile solution at 253  $\text{cm}^{-1}$ . Two peaks were recorded in the IR spectrum of Nujol mull at 143 and 360  $\text{cm}^{-1}$  and one peak was observed at 358  $\text{cm}^{-1}$  in acetonitrile solution. The spectra strongly indicated a tetrahedral structure for  $\text{MgCl}_4^{2-}$  anion.

Brooker<sup>14</sup> studied Raman spectra of single crystals of  $\text{K}_2\text{MgCl}_4$  and  $\text{Cs}_2\text{MgCl}_4$  at 77 and 298 K, his data were in good agreement with factor group analysis on the space group  $I4/mmm$  ( $D_{4h}^{17}$ ) and  $\text{Pnma}$  ( $D_{2h}^{16}$ ) for

$K_2MgCl_4$  and  $Cs_2MgCl_4$  crystals. The data suggested that the coordination number of magnesium changed from six in solid  $K_2MgCl_4$  to four in the melt, and the existence of tetrahedral species  $MgCl_4^{2-}$  in solid and molten  $Cs_2MgCl_4$ . The presence of discrete  $MgCl_4^{2-}$  species was supported from the high resolution study of  $\nu_1$  region at 77 K, where the  $Cl^{35}$ ,  $Cl^{37}$  isotope splitting was clearly resolved and found to be similar to  $CCl_4$ . Bands were observed at 271.9, 270.3, 268.0, and 266.4  $cm^{-1}$  with relative intensities 37%, 42%, 17%, 4.6%, and 0% due to  $Mg^{35}Cl_4^{2-}$ ,  $Mg^{35}Cl_3^{37}Cl^{2-}$ ,  $Mg^{35}Cl_2^{37}Cl_2^{2-}$ ,  $Mg^{35}Cl^{37}Cl_3^{2-}$  and  $Mg^{37}Cl_4^{2-}$  respectively. The Raman spectra of the molten salts strongly indicated that  $MgCl_4^{2-}$  is the predominant species in the melts. A peak was observed around 225  $cm^{-1}$  in the melts of  $K_2MgCl_4$  and  $Cs_2MgCl_4$ , and the intensity of this peak decreased by increasing the temperature. This peak was attributed to the presence of another species in the form of polynuclear complex  $Mg_2Cl_6^{2-}$ . It was suggested that the reduction in the intensity of that peak is consistent with the breaking up of the polynuclear complex and the formation of more  $MgCl_4^{2-}$  ions.

The Raman spectra of  $MgCl_2$  in the melt at 1010 K and in the solid at 77 K and 298 K have been studied<sup>15</sup>. The two peaks observed in the solid state spectrum were identical to the ones observed by Capwell<sup>10</sup>. It was suggested that  $MgCl_2$  does not undergo any phase transition between 77 K and the melting point. Four peaks were detected in the  $I_{||}$  spectrum of the melt around 130, 194, 244, and 335  $cm^{-1}$  respectively, and three peaks were detected in the  $I_{\perp}$  spectrum of the melt, one broad peak at 335  $cm^{-1}$  and another two weak peaks around 100 and 140  $cm^{-1}$ . On the basis of the relative intensity and polarization characteristics, the peaks at 335, 244, 140, and 100  $cm^{-1}$  were assigned to the  $\nu_3$ ,  $\nu_1$ ,  $\nu_4$  and  $\nu_2$  vibrations of the discrete  $MgCl_4^{2-}$  tetrahedral



structure. The peaks at 194 and 130  $\text{cm}^{-1}$  were attributed to symmetric stretching vibrations of a polynuclear complex  $\text{Mg}_2\text{Cl}_n^{4-n}$ . The Raman spectra suggested that  $\text{MgCl}_2$  does not melt with retention of the basic lattice structure as was suggested before<sup>10</sup> but melts to give a dynamic equilibrium mixture containing  $\text{MgCl}_4^{2-}$ , polynuclear complexes, and  $\text{Mg}^{2+}$  and  $\text{Cl}^-$  ions. On comparing the intensities of the peaks observed in  $\text{K}_2\text{MgCl}_4$  melt<sup>14</sup> and  $\text{MgCl}_2$  melt in the region 170-270  $\text{cm}^{-1}$ , it was concluded that the decrease in the intensity ratio of the peaks at 244 and 194  $\text{cm}^{-1}$ , i.e.  $I_{244}/I_{194}$ , in  $\text{MgCl}_2$  melt is consistent with a decrease in the concentration of  $\text{MgCl}_4^{2-}$  as the  $\text{Cl}^-$  concentration decreased and a corresponding increase in polynuclear complex.

The Raman spectra of  $\text{CsMgCl}_3$  and  $\text{Cs}_3\text{MgCl}_5$  in the solid state and as single crystals have been studied.<sup>16</sup>  $\text{CsMgCl}_3$  has space group  $\text{P6}_3/\text{mmc}(\text{D}_{6h}^4)$ , five Raman active modes were predicted,  $A_{1g}$ ,  $E_{1g}$  and  $3E_g$ . The Raman results were in excellent agreement with these predictions from factor group analysis. The Raman spectra were also obtained at 77 K, and the results indicated that no phase transition occurs between room temperature and 77 K. The Raman results of  $\text{Cs}_3\text{MgCl}_5$  indicated that discrete  $\text{MgCl}_4^{2-}$  tetrahedral species are present, and the peak positions in the solid state are quite similar to the molten salt values:  $\nu_1(A_1) \sim 250 \text{ cm}^{-1}$ ;  $\nu_2(E) \sim 120 \text{ cm}^{-1}$ ;  $\nu_3(T_2) \sim 350 \text{ cm}^{-1}$  and  $\nu_4(T_2) \sim 140 \text{ cm}^{-1}$ . The results of the oriented single crystal studies were in excellent agreement with the predictions of the factor group analysis based on the space group  $\text{I4}/\text{mcm}(\text{D}_{4h}^{18})$ . Both  $\text{Cs}_3\text{MgCl}_5$  and  $\text{Cs}_2\text{MgCl}_4$  contain the discrete  $\text{MgCl}_4^{2-}$  tetrahedral units, the results conclusively showed that  $\text{Cs}_3\text{MgCl}_5$  has a distinct structure different from  $\text{Cs}_2\text{MgCl}_4$ <sup>14</sup> and this structural difference



could be deduced from the difference in the Raman spectra.

Raman spectra in the solid and molten states of composition  $\text{MgCl}_2 + n\text{ACl}$  ( $n = 0-4$  and  $A = \text{Cs, Rb, K, Na, Li}$ ) have been studied.<sup>17</sup> Characteristic spectra were observed for each of the predicted double salts, and the results were in excellent agreement with phase diagram studies. The Raman results on the alkali metal-rich region of  $\text{RbCl-MgCl}_2$  and  $\text{KCl-MgCl}_2$  suggested the presence of a new incongruent melting compounds  $\text{Rb}_3\text{MgCl}_5$  and  $\text{K}_3\text{MgCl}_5$ . The results suggested that the compounds  $\text{Cs}_2\text{MgCl}_4$ ,  $\text{Cs}_3\text{MgCl}_5$  and  $\text{Rb}_3\text{MgCl}_5$  contain the discrete  $\text{MgCl}_4^{2-}$  tetrahedral ion, and the other solids contain distorted network octahedra with face-, edge-, or corner-shared chlorides. Raman spectra of the melts were characterized by three depolarized peaks at about 110, 145, and  $350\text{ cm}^{-1}$  and one polarized peak in the  $200-250\text{ cm}^{-1}$  region. By comparing the melts of low  $\text{MgCl}_2$  concentration, a marked cation dependence on the polarized band was observed, the peak maximum was shifted to slightly lower frequencies and the halfwidth of the band increased over the cation series  $\text{Cs}^+$  to  $\text{Li}^+$ . This was attributed to the fact that the small  $\text{Li}^+$  ion can compete quite favourably for the chloride ion which decreases the  $\text{Mg-Cl}$  force constant and reduces the frequency. An additional Raman peak at  $\sim 225\text{ cm}^{-1}$  was clearly observed for Cs, Rb, and K salts by increasing the  $\text{MgCl}_2$  concentration. This peak was attributed to the formation of new equilibrium species in the melts of high  $\text{MgCl}_2$  concentration. By analogy with the low melting  $\text{CsCl-AlCl}_3$  system where two peaks at 350 and  $312\text{ cm}^{-1}$  were clearly resolved and have been assigned to  $\text{AlCl}_4^-$  and  $\text{Al}_2\text{Cl}_7^-$  ions on the basis of concentration studies and normal coordinate analysis, it was proposed that the polarized peak at  $225\text{ cm}^{-1}$  is due to the  $\text{Mg}_2\text{Cl}_7^{3-}$  ion on the

fact that the magnesium can retain its tetrahedral coordination through corner-sharing with other magnesium centered tetrahedrons. Also an edge-shared  $\text{Mg}_2\text{Cl}_6^{2-}$  was proposed, but the formation of  $\text{Mg}_2\text{Cl}_7^{3-}$  was considered more favourable.

The Raman spectra of  $\text{MnCl}_2$  as a single crystal have been investigated<sup>18</sup>. Two Raman active modes  $A_{1g}$  and  $E_g$  were predicted from factor group analysis based on the space group  $R\bar{3}m(D_{3d}^5)$ . Two bands were observed at 234.5 and 144  $\text{cm}^{-1}$  and assigned to  $A_{1g}$  and  $E_g$  modes. The assignment is consistent with polarization characteristic and Raman results on isomorphous  $\text{MgCl}_2$ <sup>10,15</sup>. Two peaks were observed in the IR spectrum at 180 and 230  $\text{cm}^{-1}$  and assigned to  $A_{2u}$  and  $E_u$  modes.

The Raman spectra of molten  $\text{MnCl}_2$ -KCl system have been studied<sup>19</sup> at various compositions. One totally symmetric stretching mode was observed in the range from 100  $\text{cm}^{-1}$  to 400  $\text{cm}^{-1}$  for every melt, and the other vibrational frequencies were not observed because of their low intensities and a limited sensitivity of the spectrophotometer. It was observed that the polarized peak in molten  $\text{MnCl}_2$  (mol fraction  $x = 1.0$ ) appeared at 208  $\text{cm}^{-1}$ , and the frequency of this peak increase with increased KCl content until it reach 251  $\text{cm}^{-1}$  for specimen of  $x = 0.4$ , then it slightly decrease to 245  $\text{cm}^{-1}$  for the specimen of  $x = 0.1$ . The increase of the Raman frequency of the polarized peak was attributed to the dissociation of the  $(\text{MnCl}_2)_n$  species upon the addition of KCl to  $\text{MnCl}_2$ , and the formation of  $\text{MnCl}_6^{4-}$  octahedral units was suggested from comparison with  $(\text{MnCl}_2)_n$  species in pure  $\text{MnCl}_2$ . The existence of a small amount of  $\text{MnCl}_4^{2-}$  ions was suggested upon the observation of a slight shoulder at  $\sim 250 \text{ cm}^{-1}$  in the spectra of the melts,  $x = 1.0, 0.9$ , and 0.8. The existence of the tetrahedral  $\text{MnCl}_4^{2-}$  ions was proposed as



the predominant species in the region of  $x = 0.2$  to  $x = 0.4$ . Also in this composition range the formation of other types of complex ions such as the pyramidal  $\text{MnCl}_3^-$  ion or  $\text{Mn}_2\text{Cl}_7^{3-}$  was suggested. The presence of an equilibrium between discrete species with characteristic peaks was not confirmed by the present study.

The structure of some chloride complexes of 3d metals have been investigated in the molten salts<sup>20</sup>. The Raman spectra of melts of  $\text{MnCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{ZnCl}_2$ , and  $\text{CuCl}_2$  in  $\text{CsCl}$ ,  $\text{CsCl-NaCl}$  eutectic, and  $\text{LiCl-KCl}$  eutectic were recorded. For  $\text{MnCl}_2$  system and  $\text{CoCl}_2$  system, two peaks were observed, one polarized peak in the region  $240-280 \text{ cm}^{-1}$  assigned to  $\nu_1(A_1)$  mode of  $T_d$  symmetry, and another peak in the region  $120-130 \text{ cm}^{-1}$  attributed to the deformation vibration  $\nu_4(T_2)$ . For the  $\text{NiCl}_2$  and  $\text{ZnCl}_2$  systems, one band was observed in the range  $260-275 \text{ cm}^{-1}$  and attributed to the totally symmetric vibration  $\nu_1(A_1)$ . Three weak peaks at  $270$ ,  $150$  and  $125 \text{ cm}^{-1}$  were observed for a melt of 1 mole %  $\text{CuCl}_2$  in  $\text{CsCl-NaCl}$  eutectic, the first peak was attributed to  $\nu_1(A_1)$  symmetrical vibration and the other two peaks attributed to  $B_2$  and  $E$  modes on the assumption of  $D_{2d}$  symmetry.

Molten mixtures of  $\text{MnCl}_2\text{-AlCl}_3$  and  $\text{MnCl}_2\text{-CsCl}$  were investigated by electronic absorption spectroscopy and Raman spectroscopy<sup>23</sup>. For the melt of  $\text{MnCl}_2\text{-AlCl}_3$ , it was suggested that the  $\text{Mn}^{2+}$  was octahedrally coordinated to  $\text{AlCl}_4^-$  or  $\text{Al}_2\text{Cl}_7^-$  groups. The Raman results supported strongly the formation of separate tetrahedral  $\text{MnCl}_4^{2-}$  units in mixtures of  $\text{MnCl}_2$  with excess  $\text{CsCl}$ .

The Raman spectra of  $\text{MnCl}_2\text{-2ACl}$  melts have been studied<sup>24</sup>. A single polarized peak was observed in the frequency region  $100-400 \text{ cm}^{-1}$  for every melt, and the other peaks were not observed because of their



low intensities and the limited sensitivity of the spectrophotometer. It was found that the peak position  $\nu_1$  was nearly the same for every melt, and the halfwidths of the peak  $\Delta\nu$  varied moderately over the cation series  $\text{Cs}^+$  to  $\text{Li}^+$ . It was concluded that the type of complex ion in each  $\text{MnCl}_2 \cdot 2\text{ACl}$  melt was  $\text{MnCl}_4^{2-}$  with  $\nu_1 \approx 249 \text{ cm}^{-1}$ .

Bues<sup>25</sup> investigated  $\text{CdCl}_2$ -KCl melts, he favored a triangular planar of  $D_{3h}$  structure. Tanaka et. al.<sup>26</sup> examined the  $\text{CdCl}_2$ -KCl system. Four peaks were recorded at 257, 211, 245, and  $177 \text{ cm}^{-1}$ , and assigned to  $\nu_1(A_1)$ ,  $\nu_2(A_1)$ ,  $\nu_3(E)$ , and  $\nu_4(E)$ . The assignment was based on comparison of the data obtained from the corresponding solid system. It was concluded that pyramidal  $\text{CdCl}_3^-$  was the predominant species in the melt because two Raman peaks were attributed to polarized peaks  $\nu_1(A_1)$  and  $\nu_2(A_1)$ , among the four observed peaks.

The Raman spectra for  $\text{CdCl}_2$ -KCl melts containing 65, 50, and 35 mole %  $\text{CdCl}_2$  in KCl have been investigated by Maroni and Hathaway<sup>27</sup>. The spectrum of the sample containing 35 mole %  $\text{CdCl}_2$  was not different from that of the sample containing 50 mole %  $\text{CdCl}_2$ . A broad polarized envelope centered at  $230 \text{ cm}^{-1}$  was observed for the sample containing 65 mole %  $\text{CdCl}_2$ , and it was suggested that this broad envelope contain two peaks one at  $259 \text{ cm}^{-1}$  and a second peak associated with polynuclear aggregate. One polarized peak was recorded at  $259 \text{ cm}^{-1}$  for the sample containing 50 mole %  $\text{CdCl}_2$ . The polarized Raman peak observed at  $259 \text{ cm}^{-1}$  was attributed to a totally symmetric stretching vibration for tetrahedral  $\text{CdCl}_4^{2-}$ , or planar  $\text{CdCl}_3^-$ , or pyramidal  $\text{CdCl}_3^-$ . A shoulder was observed at  $80 \text{ cm}^{-1}$  and attributed to the bending mode. It was concluded that the Raman spectra of  $\text{CdCl}_2$ -KCl melts were incomplete in terms of the assumed structures for  $\text{CdCl}_4^{2-}$  or  $\text{CdCl}_3^-$  species but not inconsistent with any of the proposed structures.

Clarke et. al.<sup>28</sup> studied the Raman spectra of molten cadmium halides and their molten mixtures with alkali metal halides. They concluded that pure molten cadmium halide has octahedral coordination of  $\text{Cd}^{+2}$ , and the addition of alkali metal halides results in the replacement of octahedral by tetrahedral  $\text{Cd}^{+2}$  coordination sites.

The structure of molten  $\text{MnCl}_2$  has been examined by x-ray diffraction<sup>29</sup>. The radial distribution function of  $\text{MnCl}_2$  melt was obtained, and a fit to a structural model deduced from possible geometrical orientation among the ions. It was concluded that the coordination number and the nearest distance of the Mn-Cl pair in  $\text{MnCl}_2$  melt are about 4.0 and  $2.51 \text{ \AA}$ . A f.c.c. structural model was proposed with loosely distributed Cl atoms with tetrahedral coordination of each Mn atoms. A contribution to the structure from small fraction of octahedrally coordinated Mn could not be ruled out.

Ohno et. al.<sup>30</sup> investigated the structure of molten  $\text{MnCl}_2 \cdot 2\text{LiCl}$  and  $\text{MnCl}_2 \cdot 2\text{KCl}$  by consideration of the radial distribution function. The results indicated that the number of nearest neighbour Mn-Cl pairs of molten  $\text{MnCl}_2 \cdot 2\text{KCl}$  and  $\text{MnCl}_2 \cdot 2\text{LiCl}$  is 4.0. The data confirmed the existence of  $[\text{MnCl}_4]^{2-}$  tetrahedral units in molten  $\text{MnCl}_2 \cdot 2\text{KCl}$  and  $\text{MnCl}_2 \cdot 2\text{LiCl}$ .

Kleppa and McCarty<sup>31</sup> measured the enthalpies of mixing in  $\text{MgCl}_2$ -Alkali chloride systems, except the  $\text{LiCl-MgCl}_2$  system, they found a very marked dip in the interaction parameter,  $\Delta H/\chi(1-\chi)$ , at  $x_{\text{MgCl}_2} = 0.33$  which is the concentration corresponding to the formula  $\text{A}_2\text{MgCl}_4$ . The enthalpy data were interpreted to support the view first suggested by Flood and Urnes<sup>32</sup> that the alkali chloride-magnesium chloride systems contain the complex anionic species  $\text{MgCl}_4^{2-}$ . The stability of this



species depends strongly on the alkali cation, and increases from Lithium to Cesium. Østvold<sup>33</sup> made e.m.f. measurements in  $\text{MgCl}_2$ -Alkali chloride mixtures using glass membrane cells, the entropy curves showed inflection points at  $x_{\text{MgCl}_2} = 0.33$ . This was accounted for in terms of the presence of an ordered structure in these melts at the composition  $x_{\text{MgCl}_2} = 0.33$ . Papatheodorou and Kleppa<sup>34</sup> have measured calorimetrically the heats of mixing in the binary systems  $\text{MnCl}_2$ - $\text{AlCl}_3$ ,  $\text{FeCl}_2$ - $\text{AlCl}_3$  and  $\text{CoCl}_2$ - $\text{AlCl}_3$ . The concentration dependence of the interaction parameters  $\Delta H_m/x_1x_2$  indicated special stabilization of these mixtures at about 33%  $\text{MCl}_2$  composition. They attributed this effect to the possible formation of a tetrahedrally coordinated  $\text{MCl}_4^{2-}$  species. Thermodynamic properties of  $\text{MnCl}_2$ - $\text{AlCl}_3$  system were studied<sup>35</sup> by emf measurements. The results were interpreted in terms of the presence of  $\text{MnCl}_4^{2-}$  complex anions.



## 2. Theory

When<sup>46</sup> monochromatic light of frequency  $\bar{\nu}_0$  is directed at a sample, most of the light passes through the sample. Some of the light is scattered by the sample molecules in all directions. Some of the scattered light has the same frequency  $\bar{\nu}_0$  as the incident light, and is called Rayleigh scattering. A small fraction of the scattered light has frequency  $\bar{\nu}_i \neq \bar{\nu}_0$ . The process of producing light of frequency other than  $\bar{\nu}_0$  is called Raman scattering. The amount of scattered light with frequency  $\bar{\nu}_i < \bar{\nu}_0$  (Stokes lines) is greater than that with frequency  $\bar{\nu}_i > \bar{\nu}_0$  (anti-Stokes lines). As a result of placing a molecule in the electric field of electromagnetic radiation, a dipole moment,  $\vec{\mu}_{ind}$ , is induced in the molecule and is proportional to the field strength ( $\vec{E}$ ):

$$\vec{\mu} = \vec{\alpha} \vec{E} \quad (2)$$

The polarizability  $\vec{\alpha}$  is a symmetric tensor containing a combination of symmetric part ( $\alpha$ ) and asymmetric part ( $\beta$ ). The scattered intensity<sup>22</sup> may be conveniently divided into two components both theoretically and experimentally, polarized and depolarized and are given by these two equations:

$$I_{\alpha} = I_{iso} = I_{pol} = I_{||} - 4/3 I_{\perp} \quad (3)$$

$$I_{\beta} = I_{aniso} = I_{depol} = I_{\perp} \quad (4)$$

$I_{||}$  is the measured intensity of scattered light polarized in the same

plane as the incident light, and  $I_{\perp}$  is the measured intensity of scattered light polarized perpendicular to the incident beam. The anisotropic spectrum  $I_{\beta}$  may be obtained directly from  $I_{\perp}$ . The isotropic spectrum may be obtained by the appropriate subtraction of  $I_{\perp}$  from  $I_{||}$  as may be seen from eqn. 3.

The observed scattered intensity is  $I_{(\bar{\nu})}^{obs}$  (either  $I_{||}$  or  $I_{\perp}$ ) and is measured directly from Raman spectrometer. However the intensity of low frequency modes is temperature dependent, and the intensity of these modes is very weak with respect to the intensity of Rayleigh scattering. The contribution from Rayleigh scattering and temperature dependence can be removed by calculation of a corrected intensity  $R_2(\bar{\nu})$  as follows<sup>21</sup>:

$$I(i) = K(\bar{\nu}_0 - \bar{\nu}_i)^4 \bar{\nu}_i^{-1} B^{-1} \left( \frac{\partial \alpha}{\partial Q_i} \right)^2 \quad (5)$$

where  $R_2(\bar{\nu}) = K \left( \frac{\partial \alpha}{\partial Q_i} \right)^2$  and represents a molar scattering efficiency

$I(i)$  is the intensity of the  $i^{th}$  fundamental

$K$  is a constant

$\bar{\nu}_i$  is the frequency of the  $i^{th}$  Raman mode in  $\text{cm}^{-1}$

$\bar{\nu}_0$  is the excitation frequency in  $\text{cm}^{-1}$

$\frac{\partial \alpha}{\partial Q_i}$  is the rate of change in mean molecular polarizability with respect to the normal coordinate,  $Q_i$

$B$  is a factor defined by the following equation

$$B = 1 - \exp(-hc\bar{\nu}_i/k_B T) \quad (6)$$

where  $k_B$  is the Boltzmann constant

$T$  is the temperature of the sample

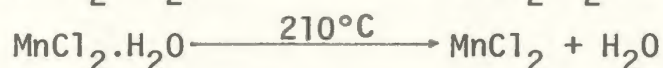
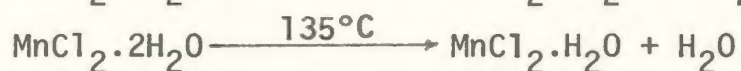
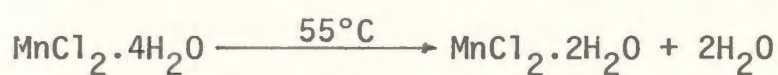
The advantage<sup>22</sup> of the  $R_2(\bar{\nu})$  spectrum is that it suppresses the central Rayleigh peak and emphasizes the Raman peaks so it is quite possible to accurately measure the low frequency region of the Raman spectrum of liquids and melts. The  $R_2(\bar{\nu})$  spectrum presents the relative molar scattering efficiencies of Raman bands directly and gives a direct spectrum of the vibrational density of states. In the study which follows both the  $I(\bar{\nu})$  and  $R_2(\bar{\nu})$  spectra have been constructed from experimental measurements.



### 3. Experimental Procedures

#### 3.1 Samples Preparation

Analytical reagent  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (BDH) was dehydrated in a vacuum oven, and the temperature was raised slowly over (10 hours) to  $180^\circ\text{C}$ . Dehydration was continued in another oven under vacuum at  $210^\circ\text{C}$  for 40 hours until all water of hydration has been removed. The dehydrated salt was obtained according to the following equations<sup>36</sup>:



$\text{MgCl}_2$  (Alpha) was dried under vacuum at  $30^\circ\text{C}$  for 24 hours, then the temperature was raised slowly to  $180^\circ\text{C}$  where the solid was further dried under vacuum.

Spectrographic grade  $\text{CsCl}$  and  $\text{RbCl}$  (Fisher) were dried under vacuum at  $180^\circ\text{C}$  for 24 hours.

Reagent grade  $\text{KCl}$  and  $\text{NaCl}$  (Anachemia) were recrystallized twice from doubly distilled water and then dried under vacuum at  $210^\circ\text{C}$  for 24 hours.

Reagent grade  $\text{LiCl} \cdot \text{H}_2\text{O}$  (BDH) was recrystallized twice from doubly distilled water and then dehydrated under vacuum, and the temperature was raised slowly to  $120^\circ\text{C}$ . Dehydration was continued at  $210^\circ\text{C}$  for 24 hours until the anhydrous  $\text{LiCl}$  was obtained.

For  $\text{MnCl}_2$ -Alkali chloride mixtures, the following samples were prepared according to the appropriate ratios:

- $\text{CsMnCl}_3$ ,  $\text{Cs}_2\text{MnCl}_4$ ,  $\text{Cs}_3\text{MnCl}_5$ ,  $\text{CsMn}_4\text{Cl}_9$   
 $\text{CsCl}:\text{MnCl}_2$  (1:2),  $\text{CsCl}:\text{MnCl}_2$  (1:3.5)

$\text{CsCl}:\text{MnCl}_2$  (1:4.5)

-  $\text{RbMnCl}_3$ ,  $\text{Rb}_2\text{MnCl}_4$ ,  $\text{Rb}_3\text{Mn}_2\text{Cl}_7$

$\text{RbCl}:\text{MnCl}_2$  (3:1),  $\text{RbCl}:\text{MnCl}_2$  (4:1)

-  $\text{KMnCl}_3$ ,  $\text{K}_3\text{Mn}_2\text{Cl}_7$ ,  $\text{K}_4\text{MnCl}_6$

$\text{KCl}:\text{MnCl}_2$  (2:1),  $\text{KCl}:\text{MnCl}_2$  (3:1)

-  $\text{NaMnCl}_3$ ,  $\text{Na}_2\text{MnCl}_4$ ,  $\text{Na}_2\text{Mn}_3\text{Cl}_8$ ,  $\text{NaMn}_4\text{Cl}_9$ ,  $\text{Na}_6\text{MnCl}_8$

$\text{NaCl}:\text{MnCl}_2$  (3:1)

-  $\text{LiCl}:\text{MnCl}_2$  (1:1),  $\text{LiCl}:\text{MnCl}_2$  (2:1),  $\text{LiCl}:\text{MnCl}_2$  (3:1)

For  $\text{MgCl}_2$  - Alkali chloride mixtures, the following samples were prepared according to the appropriate ratios:

-  $\text{CsMgCl}_3$ ,  $\text{Cs}_2\text{MgCl}_4$

$\text{CsCl}:\text{MgCl}_2$  (1.5:1),  $\text{CsCl}:\text{MgCl}_2$  (0.5:1),  $\text{CsCl}:\text{MgCl}_2$  (4:1)

-  $\text{KMgCl}_3$ ,  $\text{K}_2\text{MgCl}_4$

$\text{KCl}:\text{MgCl}_2$  (1.5:1),  $\text{KCl}:\text{MgCl}_2$  (0.5:1)

The appropriate quantities of the salts were placed in 4 mm i.d. quartz tubes, heated under vacuum such that temperature was raised slowly to  $210^\circ\text{C}$ , maintained at this value for at least 24 hours, and then the temperature slowly raised until the salt mixtures melted. The salts and the salt mixtures are hygroscopic so all manipulation were performed in a glove box under dry Nitrogen. After melting the salt mixtures, the melts of  $\text{MnCl}_2$  samples were clear yellow liquids and showed no evidence of any impurities. The melts of  $\text{MgCl}_2$  samples were colorless liquids and showed no evidence of any impurity such as solid  $\text{MgO}$ . The samples were cooled to room temperature and sealed under vacuum. It appeared that each salt could be characterized by its Raman spectrum since at least one peak occurred for each compound in the region of stability predicted by the phase diagram. Except for one



sample of  $\text{CsMgCl}_3$  which was not properly sealed the sample gave reproducible Raman spectra even after an interval of several months.

### 3.2 Characterization of the Solids

Each solid was characterized by its distinct Raman spectrum. Attempts were made to characterize the solid compounds through X-ray diffraction powder patterns. Powder patterns were obtained for powdered samples sealed in Lindemann tubes by Debye-Scherrer camera methods both at the Earth Science Department, Memorial and at AECL, Pinawa. The results were not very encouraging because the samples deteriorated rapidly in the transfer process from the quartz Raman tube into the Lindemann tube. It was obvious that even in a dry box the grinding operation gave sufficient time and surface area for absorption of considerable water. Powder patterns of  $\text{RbMnCl}_3$  and  $\text{Rb}_2\text{MnCl}_4$  which agreed with the literature were obtained but the powder patterns for  $\text{CsMnCl}_3$  and  $\text{Cs}_2\text{MnCl}_4$  had deteriorated to those of the hydrated salts. Raman and infrared spectra of  $\text{CsMnCl}_3$  and  $\text{Cs}_2\text{MnCl}_4$  from the opened samples also revealed the presence of water of hydration. No attempts were made to obtain powder patterns for the other samples since it would have necessitated destroying the samples prepared for Raman studies.

### 3.3 Raman Spectroscopic Measurements

#### 3.3.1 Molten Phase

Raman spectra were collected digitally with a Coderg PHO spectrometer. The melts of  $\text{MnCl}_2$  and  $\text{MnCl}_2$ -Alkali Chloride were recorded



after sample excitation with the 6471 Å (150 mw) and 5682 Å (100 mw) lines of Coherent Laser model 52 Krypton-Argon ion laser or a Control Laser model 552 Krypton ion laser with slit width 2 cm<sup>-1</sup>. The scan rate was 50 cm<sup>-1</sup>/min., and the photon counts were accumulated for 0.01 min. Ten scans were collected in both parallel X(ZZ)Y and perpendicular X(ZX)Y orientations, and the digital output recorded on a disk at the M.U.N. Computer Services VAX-11/780. The spectra were averaged, baseline corrected and converted into the R<sub>2</sub> format. The spectra were then plotted on a TEKTRONIX 4662 digital interactive plotter with the aid of a TEKTRONIX 4051 graphics terminal. Subtraction files were created by subtracting I<sub>⊥</sub> (perpendicular) data from I<sub>||</sub> (parallel) data to obtain the isotropic Raman spectra  $I_{iso} = I_{||} - 4/3 I_{\perp}$ .

The melts of MgCl<sub>2</sub> and MgCl<sub>2</sub>-CsCl mixtures were recorded digitally after sample excitation with the 4880 Å (500 mw) line of Control Laser model 553 Argon ion laser with slit width 2 cm<sup>-1</sup>. The melts of MgCl<sub>2</sub>-KCl system were measured after sample excitation with the 4880 Å (500 mw) line of Control Laser model 552 Argon ion laser with slit width 4 cm<sup>-1</sup>. Ten scans were collected for each orientation. The scan rate was 50 cm<sup>-1</sup>/min. and the photon counts were accumulated for 0.01 min. for the melts except for MgCl<sub>2</sub> and CsCl:MgCl<sub>2</sub> (4:1) melts the counts were accumulated for 0.02 min. The output spectra were recorded on a computer disk, averaged, baseline corrected, and converted into the R<sub>2</sub> format. The spectra were plotted using the TEKTRONIX devices. Subtraction files were created to obtain isotropic Raman spectra.

All Raman spectra of the melts were viewed and analyzed in the I( $\bar{\nu}$ ) and R<sub>2</sub>( $\bar{\nu}$ ) formats. The isotropic spectra in both formats (i.e., I<sub>α</sub>( $\bar{\nu}$ ) and R<sub>2α</sub>( $\bar{\nu}$ )) were subject to detailed band deconvolution analysis

with a program called FITTER. Both Lorentzian and a Gaussian\*Lorentzian product function were employed for each data set but detailed analysis were not very sensitive to the type of function. The best fit data are reported along with the function type.

The  $\text{MgCl}_2 \cdot n\text{ACl}$  data for  $n \geq 1$  gave clear indication of at least three polarized components in the symmetric stretching region and the curve analysis was restricted to three band fits. Two band fits gave inconsistent results. For  $n < 1$  additional low frequency intensity was obvious and a fourth band was employed. For the magnesium system the  $I_\alpha(\bar{\nu})$  spectra gave the most consistent results and these results are reported. The  $R_2(\bar{\nu})$  spectra seemed to overemphasize the weak broad high frequency component centered at about  $300 \text{ cm}^{-1}$ . Because of the complexity of the spectra the best fit data reported may not be unique. The peak frequencies of the components are probably accurate to  $\pm 2 \text{ cm}^{-1}$  but the error in halfwidths and intensities is difficult to estimate and for this reason only the trends of the three major components at about 210, 250 and  $300 \text{ cm}^{-1}$  would appear significant for samples with  $n \leq 2$ . For  $n > 2$  the peak frequency and halfwidth of the single component is probably accurate to  $\pm 1 \text{ cm}^{-1}$ .

The  $\text{MnCl}_2 \cdot n\text{ACl}$  data for  $n \geq 1$  gave no indication of more than one polarized component. Two band fits were not significantly better than one band fits. Reasonable fits were obtained for both the  $I_\alpha(\bar{\nu})$  and  $R_{2\alpha}(\bar{\nu})$  formats and the one band fits for the  $R_{2\alpha}(\bar{\nu})$  spectra are reported. For  $\text{MnCl}_2 \cdot n\text{NaCl}$  melts ( $n \geq 1$ ) a broad low frequency component  $\sim 150$ - $230 \text{ cm}^{-1}$  was apparent and a second peak was necessary to fit the data. Because of the breadth and uncertainty of this peak it was not considered significant and could be an artifact of the subtraction routine. The peak frequencies and halfwidths for the intense single component about  $250 \text{ cm}^{-1}$  are probably accurate to  $\pm 2 \text{ cm}^{-1}$ .



The spectra of the melts were obtained from samples in a furnace with the inner core wound with nichrome heating coil. The temperatures were monitored with a Chromel-Alumel thermocouple on the sample container as shown (Fig. 1). The thermocouple was calibrated with ice, boiling water and known phase transitions. Temperatures are probably accurate to about 1%.

Plasma lines were removed with the appropriate interference filter for each exciting line. Depolarization measurements for the melts were made by analyzing the scattered light parallel  $X(ZZ)Y [I_{||}]$  and perpendicular  $X(ZX)Y [I_{\perp}]$  to the incident laser beam.

### 3.3.2 Solid Phase

Raman spectra were recorded with a Coderg PHO spectrometer. Spectra of yellow compounds  $Cs_2MnCl_4$  and  $Cs_3MnCl_5$  at room and liquid nitrogen temperatures and below their melting points were recorded using the yellow exciting line  $5682 \text{ \AA}$  (100 mw) of Coherent Laser model 52 Krypton-Argon ion laser with slit width  $2 \text{ cm}^{-1}$ . For  $Cs_2MnCl_4$  a possible phase change from low-temperature phase to high-temperature phase was investigated. The effect of temperature on the totally symmetric stretching vibration ( $\nu_1$ ) of  $Cs_2MnCl_4$  and  $Cs_3MnCl_5$  was recorded.

Spectra of the red compounds  $CsMnCl_3$ ,  $CsMn_4Cl_9$ ,  $Na_2Mn_3Cl_8$ , and  $NaMn_4Cl_9$  at room temperature were recorded digitally after sample excitation with the  $6764 \text{ \AA}$  (30 mw) line of Control Laser model 552 Krypton ion laser with  $4 \text{ cm}^{-1}$  slit width, while the spectra of the other samples were collected digitally at room temperature after sample excitation with the  $6471 \text{ \AA}$  (150 mw) line of Control Laser model 552 Krypton ion laser with  $4 \text{ cm}^{-1}$  slit width. Eight scans were collected for each sample, the scan rate

was  $50 \text{ cm}^{-1}/\text{min.}$ , and the photon counts were accumulated for 0.01 min. The spectra were stored on a computer disk, averaged, base line corrected and converted to  $R_2(\bar{\nu})$  format and then plotted using the TEKTRONIX devices. The  $I(\bar{\nu})$  spectra are only plotted here.

Plasma lines were removed using an interference filter for each exciting line. The colour of the sample should match the colour of the laser light to minimize absorption. The Raman spectra of the yellow compounds were measured using the exciting line  $5682 \text{ Å}$ , while the spectra of the red compounds were recorded using the exciting lines  $6471$  and  $6764 \text{ Å}$ . The visible spectra indicate that these samples have an absorption in the blue and green regions, so the exciting lines  $4880$  and  $5145 \text{ Å}$  could not be used. The exciting line  $5682 \text{ Å}$  could not be used for measuring the Raman spectra of the red compounds because these samples have an absorption in the yellow region also. The spectra of red compounds were very difficult to obtain because octahedral manganese has a very broad visible absorption which extends into the red. It is also a highly fluorescent material. Ghost peaks were observed in most of the recorded spectra because these samples are weak scatters and high gain setting were required. Improved relatively ghost free spectra could be obtained by subtraction of a ghost spectrum measured from a white blank scatterer.

### 3.4 Visible Spectroscopic Measurements

The visible spectra of the solids and the melts were obtained in the optical range  $23042$  to  $15042 \text{ cm}^{-1}$ . The spectra were recorded digitally using the Coderg PH0 spectrometer as an absorption spectrometer with a projection lamp of 300 watts (Canadian General Electric 32).

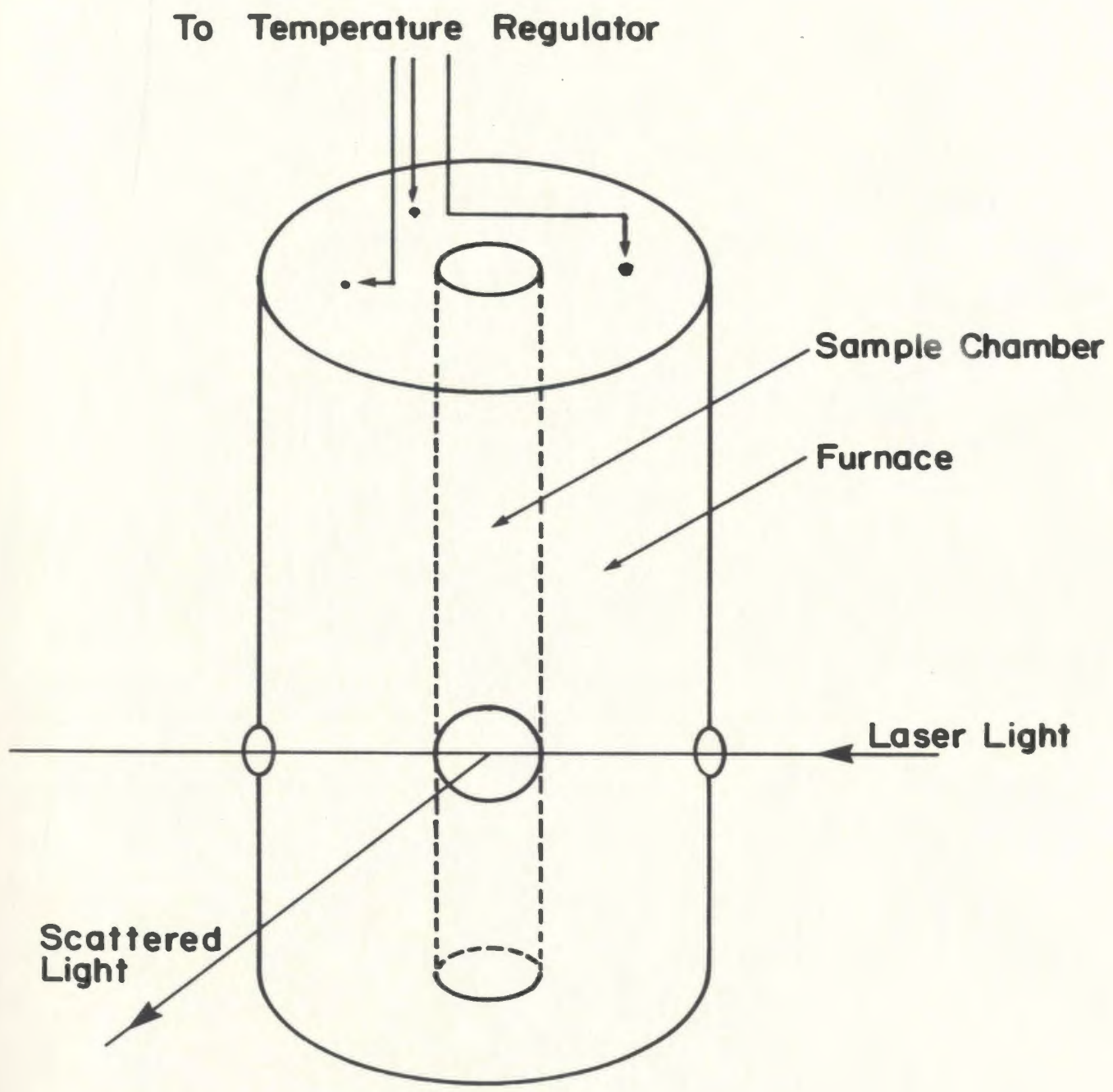


Slit widths 4 and 2  $\text{cm}^{-1}$  were employed for the solids and the melts. The spectra of the melts were obtained from samples in a furnace as shown in figure 1. The scan rate was 50  $\text{cm}^{-1}/\text{min.}$ , and the counts were accumulated for 0.04 min. One scan was collected for the projection lamp and another scan for the sample. After subtracting the two files, the subtracted file represented the visible spectrum of the sample. The relative absorbances of the visible spectra can not be directly related to the usual visible absorbance values since the spectra were obtained by different method whereas in conventional visible spectrometers the absorbance values are ratioed against the reference beam. All visible spectra were plotted on a TEKTRONIX 4662 digital interactive plotter with the aid of a TEKTRONIX 4051 graphics terminal.

Attempts were made to obtain the visible spectra using a Cary 17 spectrometer but the difficulty of maintaining the sample under dry conditions in the sample compartment prevented measurement of a satisfactory spectrum. Several attempts to melt samples into very thin glass tubes still resulted in samples that were too thick and resulted in total absorption of the incident light. The use of the Coderg PHO spectrometer with its very sensitive photomultiplier tube permitted the measurement of visible spectra of melts and solids in the same sample tubes as employed for the Raman studies.

Figure 1. Sample furnace.





#### 4. Results and Discussion

##### 4.1 Raman Studies of $\text{MnCl}_2 \cdot n\text{H}_2\text{O}$ : Solid state

###### 4.1.1 $\text{MnCl}_2$

$\text{MnCl}_2$  has the  $\text{CdCl}_2$  structure with space group  $R\bar{3}m(D_{3d}^5)$  and one molecule per unit cell. Mn atoms occupy  $D_{3d}$  site symmetry while Cl atoms occupy  $C_{3v}$  sites. Nine modes are predicted from factor group analysis and distributed as follows:

$$\begin{aligned}\Gamma_{\text{Mn}} &= A_{2u} + E_u \\ \Gamma_{\text{Cl}} &= A_{1g} + E_g + A_{2u} + E_u \\ \Gamma_{\text{total}} &= A_{1g} + E_g + 2A_{2u} + 2E_u \\ \Gamma_{\text{acoustic}} &= A_{2u} + E_u\end{aligned}\tag{7}$$

$A_{1g}$  and  $E_g$  modes are Raman active, while  $A_{2u}$  and  $E_u$  modes are IR active. The Raman spectrum of solid  $\text{MnCl}_2$  is shown in figure 2 and peak frequencies and assignments are shown in Table 1.

###### 4.1.2 $\text{MnCl}_2$ -CsCl System

The phase diagram of the  $\text{MnCl}_2$ -CsCl system<sup>37,38</sup> indicates the presence of four double salts, three congruent compounds;  $\text{CsMnCl}_3$ , melting point  $593^\circ\text{C}$ ;  $\text{Cs}_2\text{MnCl}_4$ , melting point  $538^\circ\text{C}$ ;  $\text{Cs}_3\text{MnCl}_5$ , melting point  $511^\circ\text{C}$ , and one incongruent melting  $\text{CsMn}_4\text{Cl}_9$ , melting point  $537^\circ\text{C}$ .

###### (i) $\text{Cs}_2\text{MnCl}_4$

The reports on the structure of  $\text{Cs}_2\text{MnCl}_4$  are not consistent.<sup>39,41,43,44,45</sup> It has been reported that at room temperature  $\text{Cs}_2\text{MnCl}_4$  has the  $\text{Cs}_2\text{MnBr}_4$  structure<sup>40</sup>: space group  $\text{Pnma}(D_{2h}^{16})$ , four formulas per unit cell. This structure is isomorphous with  $\text{Cs}_2\text{MgCl}_4$ <sup>42</sup> which contains discrete  $\text{MgCl}_4^{2-}$  ions. On the other hand it has been reported<sup>43,44</sup> that



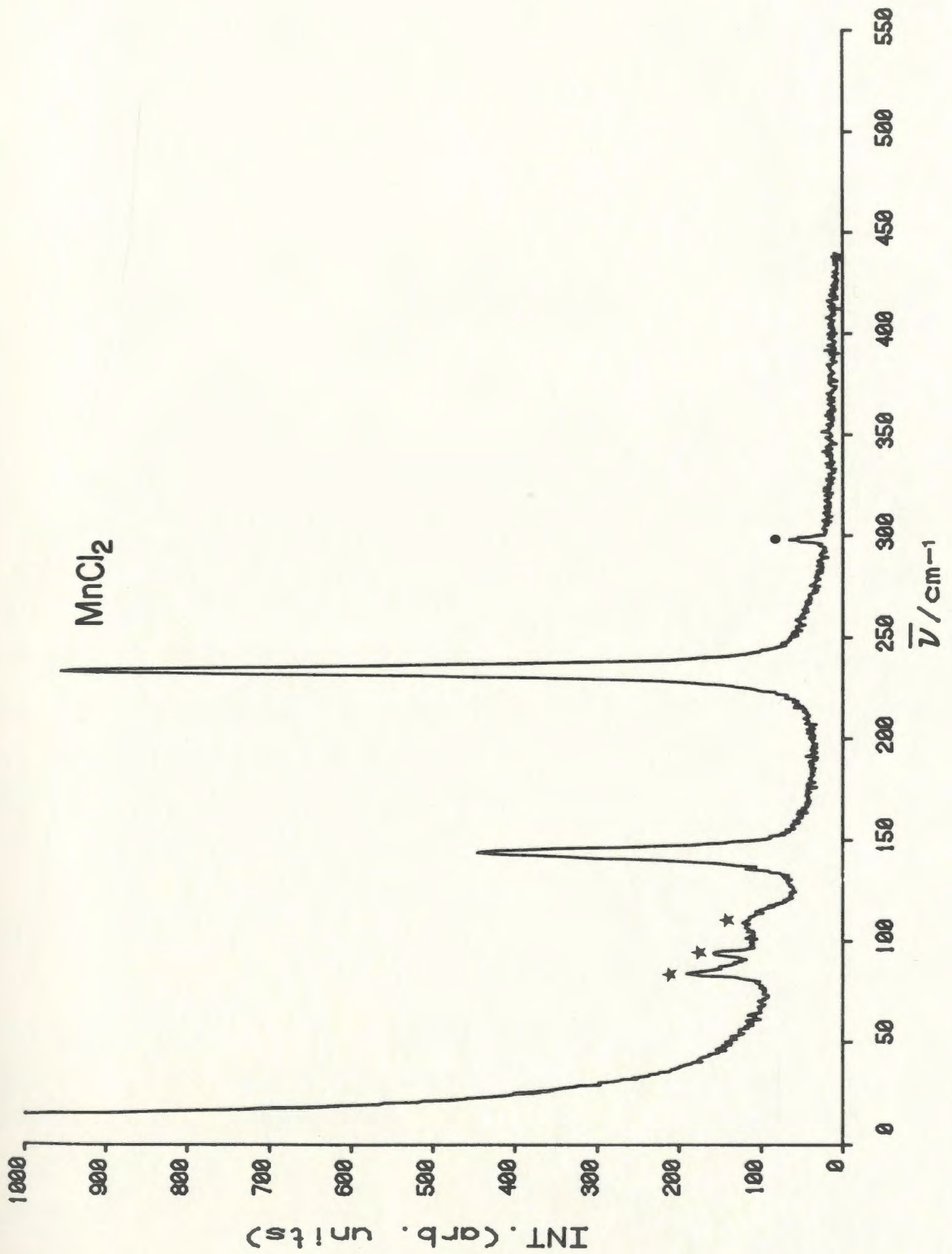
Table 1. Peak frequencies in  $\text{cm}^{-1}$  and assignments for solid  $\text{MnCl}_2$ .

Frequency	Assignments
143 m-s	$E_g$
233 v.s	$A_{1g}$

m-s: medium-strong, v.s: very strong

Figure 2. Raman spectrum of solid  $\text{MnCl}_2$  at room temperature.  
The stars indicate ghost peaks. The dot indicate  
plasma line.





$\text{Cs}_2\text{MnCl}_4$  exists in two phases; a tetragonal room temperature form called  $\alpha\text{-Cs}_2\text{MnCl}_4$  or (T-form) and an orthorhombic high temperature form stable above  $298^\circ\text{C}$  called  $\beta\text{-Cs}_2\text{MnCl}_4$  or (H-form). It has been proposed that the  $\alpha$ -form has space groups  $I4/mmm(D_{4h}^{17})$  and is isomorphous with  $\text{K}_2\text{NiF}_4$  and  $\text{K}_2\text{MgCl}_4$ <sup>42</sup> but the  $\beta$ -form has space group  $\text{Pnma}(D_{2h}^{16})$  and is isomorphous with  $\text{Cs}_2\text{ZnCl}_4$  and  $\text{Cs}_2\text{MgCl}_4$ . Seifert<sup>43,44</sup> also reported that the red  $\alpha$ -phase transformed to the yellow  $\beta$ -phase at  $298^\circ\text{C}$ . In the present study it was found that  $\text{Cs}_2\text{MnCl}_4$  had a greenish yellow color at all temperatures, and the Raman spectra of the compound obtained over a wide range of temperatures from 77 K to the melting point remained the same as long as the sample remained sealed under vacuum. Attempts were made to follow the reported<sup>75</sup>  $\alpha \rightarrow \beta$  phase transformation by thermally annealing the sample above and below the reported phase transition but no evidence of a phase transformation could be found. However if the sample was opened to the atmosphere, absorption of a small amount of water ( $\sim 0.2\%$ ) was sufficient to cause the yellow compound to turn pale red. This red compound which could be written as  $\text{Cs}_2\text{MnCl}_4 \cdot 0.16\text{H}_2\text{O}$  was very stable and the Raman spectrum indicated that this compound probably does have the  $\text{K}_2\text{NiF}_4$  structure type. Furthermore the red compound could be converted to the yellow by heating to about  $300^\circ\text{C}$ , at which point water condensed in the cold part of the tube. The Raman spectra of  $\text{Cs}_2\text{MnCl}_4$  at 77, 298 and 800 K strongly confirm the presence of discrete  $\text{MnCl}_4^{2-}$  ions and this indicate that  $\text{Cs}_2\text{MnCl}_4$  is isostructural with  $\text{Cs}_2\text{MgCl}_4$ . Most previous studies of  $\text{Cs}_2\text{MnCl}_4$  at room temperature have really been made for the hydrate  $\text{Cs}_2\text{MnCl}_4 \cdot 0.16\text{H}_2\text{O}$ .



Manganese is tetrahedrally coordinated with distinct  $\text{MnCl}_4^{2-}$  ions present in the  $\text{Cs}_2\text{MnCl}_4$  lattice. As shown from equation (1), four Raman active vibrations are expected for  $\text{MnCl}_4^{2-}$  ions, two stretching  $\nu_1(A_1)$ ;  $\nu_3(T_2)$  and two bending  $\nu_2(E)$ ;  $\nu_4(T_2)$ . These four vibrations are calculated from group theoretical prediction<sup>46,47</sup> by counting the number of unmoved atoms under each operation of the point group  $T_d$ , and multiply these numbers by the character  $\Gamma_{x,y,z}$  under each operation to obtain  $\Gamma_{\text{red.}}$  as shown in Table 2. From  $\Gamma_{\text{red.}}$ ,  $\Gamma_{\text{total}}$  and then  $\Gamma_{\text{vib.}}$  are obtained.

$$\begin{aligned}
 \Gamma_{\text{total}} &= A_1 + E + T_1 + 3T_2 \\
 \Gamma_{\text{trans}} &= T_2 \\
 \Gamma_{\text{rot}} &= T_1 \\
 \Gamma_{\text{vib}} &= A_1 + E + 2T_2 \quad (8)
 \end{aligned}$$

$\begin{array}{c} \downarrow \quad \downarrow \quad \swarrow \quad \searrow \\ \nu_1 \quad \nu_2 \quad \nu_3 \quad \nu_4 \end{array}$

A description of these vibrations<sup>48</sup> is shown in figure 3.

$\text{Cs}_2\text{MnCl}_4$  has space group  $\text{Pnma}(D_{2h}^{16})$  with four formula units per primitive unit cell, and the site symmetries of the ions are as follows:  $\text{MnCl}_4^{2-}$ ,  $C_s$ ;  $2\text{Cs}^{+1}$ ,  $C_s$ . One expect  $3.N.Z = 3.7.4 = 84$  modes distributed as follows:

Modes due to  $\text{MnCl}_4^{2-}$  ions

Internal modes = 36

Lattice modes (external modes) = 24

Modes due to  $\text{Cs}^{+1}$  ions

Lattice modes (external modes) = 24

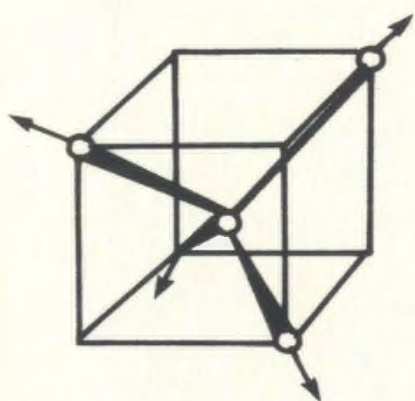
These modes are calculated using the correlation method as shown in Tables 3, 4, 5 and 6.

Table 2. Determination of  $\Gamma_{\text{red.}}$  for  $\text{MnCl}_4^{2-}$  ion.

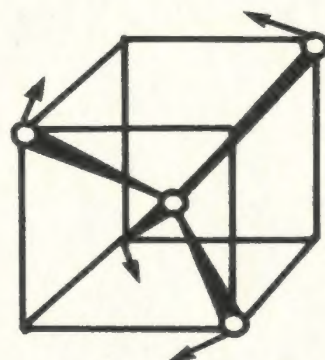
$T_d$	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
unmoved atoms	5	2	1	1	3
$\Gamma_{x,y,z}$	3	0	-1	-1	1
$\Gamma_{\text{red.}}$	15	0	-1	-1	3



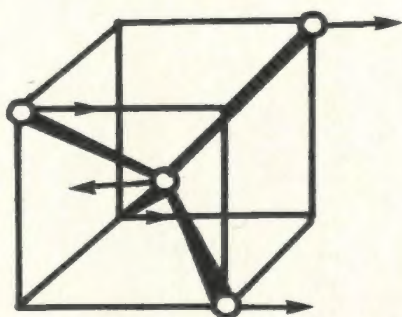
Figure 3. Normal vibrations of a tetrahedral molecule.



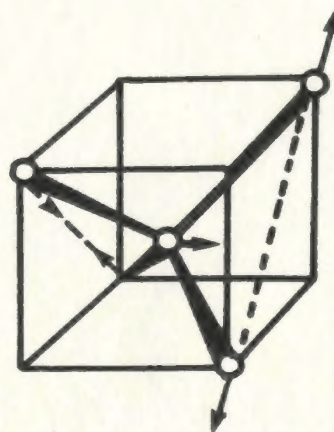
$\nu_1(A_1)$



$\nu_2(E)$



$\nu_3(T_2)$



$\nu_4(T_2)$

Table 3. Internal modes of  $\text{MnCl}_4^{2-}$  ion.

$f=Z \cdot \nu_{\text{vib}}$	$\nu_{\text{vib}}$	Molecular Symmetry ( $T_d$ )	<u>correlation</u>	Site Symmetry ( $C_s$ )	<u>correlation</u>	Space Group ( $D_{2h}$ )
4	$1(\nu_1)$	$1A_1$		$(1+1+2+2)A'$	$A_g$ 6 $B_{1g}$ 6 $B_{2u}$ 6 $B_{3u}$ 6	
8	$2(\nu_2)$	$1E$		$(1+2)A''$	$B_{2g}$ 3 $B_{3g}$ 3 $A_u$ 3 $B_{1u}$ 3	
<u>24</u>	$6(\nu_3, \nu_4)$	$2T_2$				
36 modes						36 modes



Table 4. Lattice modes of  $\text{MnCl}_4^{2-}$  ion (Translation).

$f^\gamma = Z \cdot t^\gamma$	$t^\gamma$	$C_s$ Site Symmetry species containing translation ( $\gamma$ )	<u>correlation</u>	$D_{2h}$ Space group
8	$2(T_x, T_y)$	$A'$		$A_g$ 2 $B_{1g}$ 2 $B_{2u}$ 2 $B_{3u}$ 2
4	$1T_z$	$A''$		$B_{2g}$ 1 $B_{3g}$ 1 $A_u$ 1 $B_{1u}$ 1
12 modes				12 modes

Table 5. Lattice modes of  $\text{MnCl}_4^{2-}$  ion (Rotation).

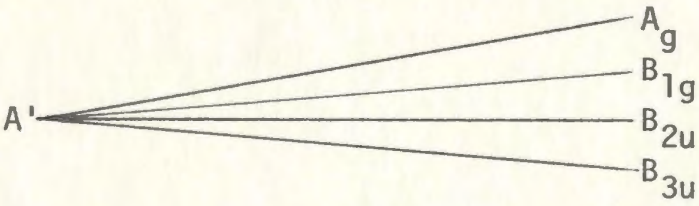
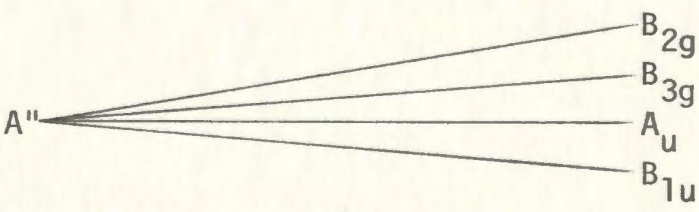
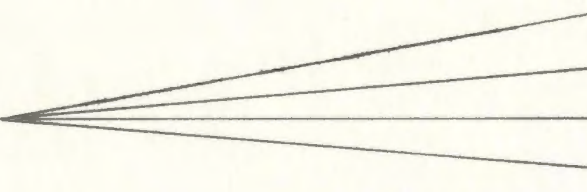
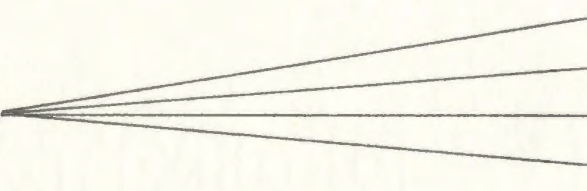
$f^\gamma = Z \cdot t^\gamma$	$t^\gamma$	$C_s$ Site Symmetry species containing rotation ( $\gamma$ )	<u>correlation</u>	$D_{2h}$ Space group
4	$1R_z$	$A'$		<div><math>A_g</math> 1</div> <div><math>B_{1g}</math> 1</div> <div><math>B_{2u}</math> 1</div> <div><math>B_{3u}</math> 1</div>
8	$2(R_x, R_y)$	$A''$		<div><math>B_{2g}</math> 2</div> <div><math>B_{3g}</math> 2</div> <div><math>A_u</math> 2</div> <div><math>B_{1u}</math> 2</div>
12 modes				12 modes

Table 6. Lattice modes of  $\text{Cs}^{+1}$  ions.

$f^{\gamma} = Z \cdot t^{\gamma}$	$t^{\gamma}$	$C_s$ Site Symmetry species containing translation ( $\gamma$ )	<u>correlation</u>	$D_{2h}$ Space group
16	$2(T_x, T_y)$	$A'$		<div><math>A_g</math> 4</div> <div><math>B_{1g}</math> 4</div> <div><math>B_{2u}</math> 4</div> <div><math>B_{3u}</math> 4</div>
8	$1T_z$	$A''$		<div><math>B_{2g}</math> 2</div> <div><math>B_{3g}</math> 2</div> <div><math>A_u</math> 2</div> <div><math>B_{1u}</math> 2</div>
24 modes				24 modes



$$\Gamma_{\text{total}} = \Gamma_{\text{MnCl}_4^{2-}} (\text{internal modes}) + \Gamma_{\text{MnCl}_4^{2-}} (\text{lattice modes}) (\text{trans.}) \\ + \Gamma_{\text{MnCl}_4^{2-}} (\text{lattice modes}) (\text{rot.}) + \Gamma_{2\text{Cs}^+1} (\text{lattice modes})$$

$$\Gamma_{\text{MnCl}_4^{2-}} \text{ internal modes} = 6A_g + 6B_{1g} + 6B_{2u} + 6B_{3u} + 3B_{2g} + 3B_{3g} + 3A_u + 3B_{1u}$$

$$\Gamma_{\text{MnCl}_4^{2-}} \text{ lattice modes (trans.)} = 2A_g + 2B_{1g} + 2B_{2u} + 2B_{3u} + B_{2g} + B_{3g} + A_u + B_{1u}$$

$$\Gamma_{\text{MnCl}_4^{2-}} \text{ lattice modes (rot.)} = A_g + B_{1g} + B_{2u} + B_{3u} + 2B_{2g} + 2B_{3g} + 2A_u + 2B_{1u}$$

$$\Gamma_{2\text{Cs}^+1} \text{ lattice modes} = 4A_g + 4B_{1g} + 4B_{2u} + 4B_{3u} + 2B_{2g} + 2B_{3g} + 2A_u + 2B_{1u}$$

$$\Gamma_{\text{total}} = 13A_g + 13B_{1g} + 13B_{2u} + 13B_{3u} + 8B_{2g} + 8B_{3g} + 8A_u + 8B_{1u} \quad (9)$$

$$\Gamma_{\text{acoustic}} = B_{2u} + B_{3u} + B_{1u}$$

As shown from equation (9) eighty-four modes are predicted, three of which are acoustic. All g modes are Raman active, all u modes are IR active, and  $A_u$  is inactive. The Raman spectra of  $\text{Cs}_2\text{MnCl}_4$  in the solid at 77, 298, and 800 K are shown in figure 4. The spectra strongly indicate the existence of the tetrahedral  $\text{MnCl}_4^{2-}$  ion. The totally symmetric vibration<sup>49</sup> ( $\nu_1$ ) of  $\text{MnCl}_4^{2-}$  has been reported in the solid at  $258 \text{ cm}^{-1}$  and in solution as a polarized line at  $251 \text{ cm}^{-1}$ . A peak due to  $\nu_4$  was reported as shoulder at  $116 \text{ cm}^{-1}$ . The present assignments have been made by analogy with spectrum of  $\text{Cs}_2\text{MgCl}_4$ <sup>14</sup>. Peak positions and assignments are shown in Table 7.

Table 7. Assignments and peak positions in  $\text{cm}^{-1}$  for solid  $\text{Cs}_2\text{MnCl}_4$ .

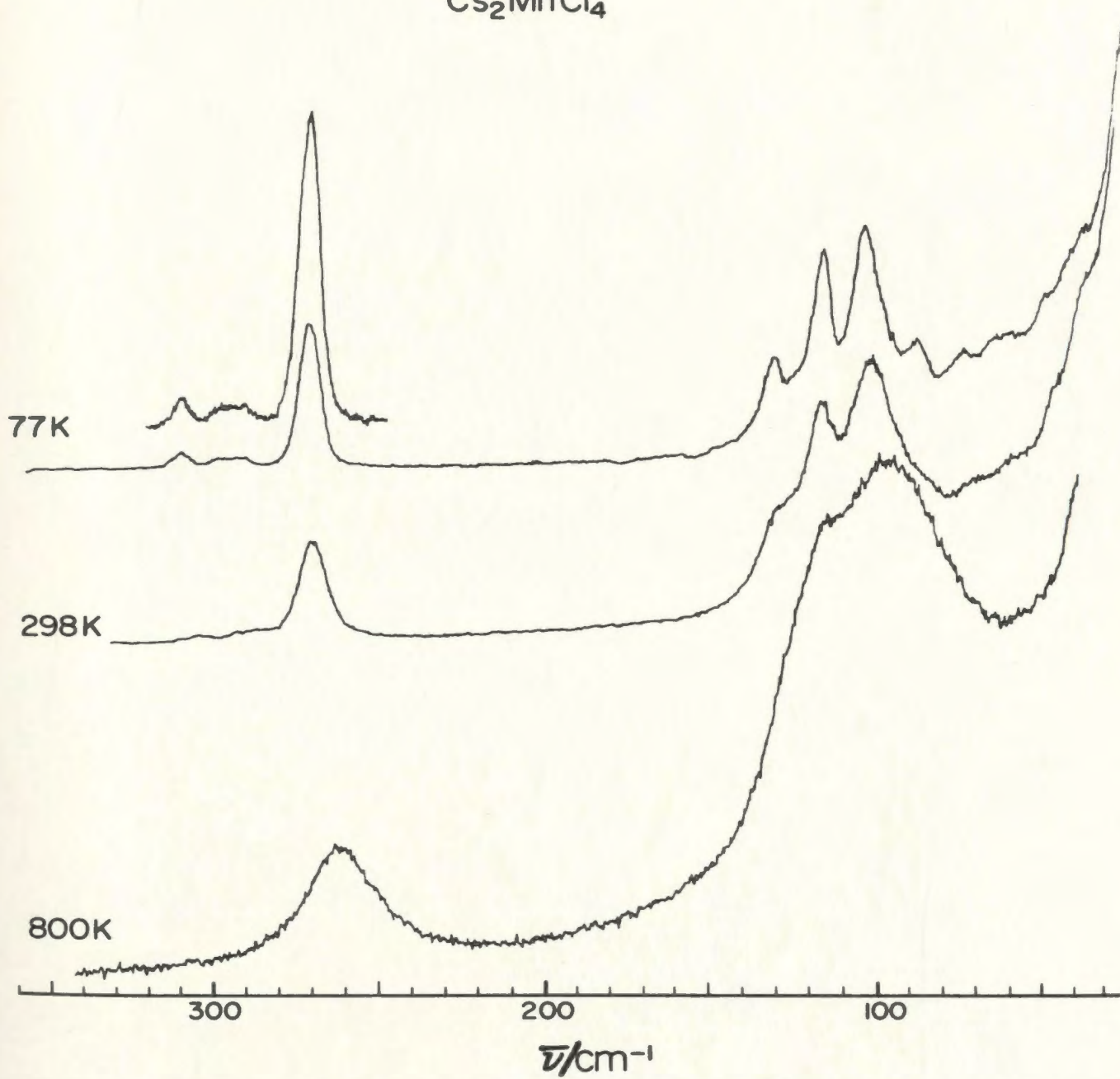
Frequency		Assignments	
77 K	298 K	800 K	
40 sh,m	39 sh,m	$B_{1g} + B_{2g} + B_{3g}$ $B_{2g}$ $A_g$ $A_g + B_{1g}$	$\left. \vphantom{\begin{matrix} B_{1g} + B_{2g} + B_{3g} \\ B_{2g} \\ A_g \\ A_g + B_{1g} \end{matrix}} \right\} \text{Lattice modes}$
51 sh,w	47 sh,m-w		
63 w	61 v.w		
75 w	72 v.w		
89 w	85 sh,v.w	$B_{2g} + B_{3g}$ $A_g$	$\left. \vphantom{\begin{matrix} B_{2g} + B_{3g} \\ A_g \end{matrix}} \right\} \nu_2$
106 m	102 m	98 m	
118 m	117 m	$B_{2g} + B_{3g}$ $A_g$	$\left. \vphantom{\begin{matrix} B_{2g} + B_{3g} \\ A_g \end{matrix}} \right\} \nu_4$
133 m-w	131 sh, m	116 s	
272 m	271 m	262 m	$A_g$ $\nu_1$
(7.5) <sup>a</sup>	(10.3)	(25)	
292 v.w	293 v.w	$A_g + B_{1g}$ $B_{2g} + B_{3g}$ $A_g + B_{1g}$	$\left. \vphantom{\begin{matrix} A_g + B_{1g} \\ B_{2g} + B_{3g} \\ A_g + B_{1g} \end{matrix}} \right\} \nu_3$
298 v.w			
310 v.w	306 v.w		

a: half band width is given in parenthesis

v.w: very weak, w: weak, m: medium, s: strong, sh: shoulder

Figure 4. Raman spectra of solid  $\text{Cs}_2\text{MnCl}_4$  at 77, 298, and 800 K.





(ii)  $\text{Cs}_3\text{MnCl}_5$

The X-ray study<sup>51</sup> on single crystal of  $\text{Cs}_3\text{MnCl}_5$  indicated that  $\text{Cs}_3\text{MnCl}_5$  is isomorphous with  $\text{Cs}_3\text{CoCl}_5$  and has space group  $I4/mcm$  ( $D_{4h}^{18}$ ) with two formula units per primitive unit cell. In the structure the Mn ion is coordinated by Cl(2) ions to form individual  $\text{MnCl}_4^{2-}$  tetrahedra, and the structure can be considered as composed of  $\text{Cs}^+$ ,  $[\text{MnCl}_4]^{2-}$  and  $\text{Cl}(1)^-$  ions. The site symmetries of the ions are as follows:  $\text{MnCl}_4^{2-}$ ,  $D_{2d}$ ;  $\text{Cs}(1)$ ,  $D_4$ ;  $\text{Cs}(2)$ ,  $C_{2v}$ ;  $\text{Cl}(1)$ ,  $C_{4h}$ .

Since the number of formulas per primitive unit cell are two, fifty-four modes are predicted from factor group analysis and distributed as follows:

- 18 modes due to internal modes of  $\text{MnCl}_4^{2-}$  ion
- 12 modes due to lattice modes of  $\text{MnCl}_4^{2-}$  ion
- 12 modes due to lattice modes of  $\text{Cs}(2)$  ion
- 6 modes due to lattice modes of  $\text{Cs}(1)$  ion
- 6 modes due to lattice modes of  $\text{Cl}(1)$  ion

$$\Gamma_{\text{total}} = \Gamma_{\text{Mn}} + \Gamma_{\text{Cl}(2)} + \Gamma_{\text{Cl}(1)} + \Gamma_{\text{Cs}(1)} + \Gamma_{\text{Cs}(2)}$$

but

$$\Gamma_{\text{Mn}} + \Gamma_{\text{Cl}(2)} = \Gamma_{\text{MnCl}_4^{2-}} (\text{internal modes}) + \Gamma_{\text{MnCl}_4^{2-}} (\text{lattice modes})$$

$$\Gamma_{\text{total}} = \Gamma_{\text{MnCl}_4^{2-}} (\text{internal modes}) + \Gamma_{\text{MnCl}_4^{2-}} (\text{lattice modes})$$

$$+ \Gamma_{\text{Cs}(1)} + \Gamma_{\text{Cs}(2)} + \Gamma_{\text{Cl}(1)}$$

$\Gamma_{\text{Cs}(1)}$ ,  $\Gamma_{\text{Cs}(2)}$ , and  $\Gamma_{\text{Cl}(1)}$  are shown in equations (10), (11), and (12).

$$\Gamma_{\text{Cs}(1)} = A_{2g} + E_g + A_{2u} + E_u \quad (10)$$

$$\Gamma_{\text{Cs}(2)} = A_{1g} + A_{2g} + B_{1g} + B_{2g} + E_g + A_{2u} + B_{1u} + 2E_u \quad (11)$$

$$\Gamma_{\text{Cl}(1)} = A_{1u} + A_{2u} + 2E_u \quad (12)$$

The internal and lattice modes for  $\text{MnCl}_4^{2-}$  ion are shown by correlation method in Tables 8, 9, and 10.

$$\Gamma_{\text{total}} = 3A_{1g} + 3A_{2g} + 2B_{1g} + 4B_{2g} + 6E_g + 2A_{1u} + 6A_{2u} + 3B_{1u} + B_{2u} + 9E_u \quad (13)$$

$$\Gamma_{\text{acoustic}} = A_{2u} + E_u$$

$B_{1u}$  and  $B_{2u}$  are inactive, all the u modes are IR active and all the g modes are Raman active according to the rule of mutual exclusion.

The Raman spectra of  $\text{Cs}_3\text{MnCl}_5$  at 77 K, 298 K, and 760 K are shown in figure 5. The spectra strongly indicate the presence of tetrahedral  $\text{MnCl}_4^{2-}$  species as suggested before<sup>23</sup>. For the totally symmetric vibration ( $\nu_1$ ), splittings are observed due to  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  isotopes. The three peaks observed at 272.5, 273.8, and 275.9  $\text{cm}^{-1}$  are assigned to  $\text{Mn}^{35}\text{Cl}_2^{37}\text{Cl}_2^{2-}$ ,  $\text{Mn}^{35}\text{Cl}_3^{37}\text{Cl}^{2-}$ , and  $\text{Mn}^{35}\text{Cl}_4^{2-}$  ions. Assignments are made by analogy with the spectrum of  $\text{Cs}_3\text{MgCl}_5$ <sup>16</sup>. Peak positions and assignments are shown in Table 11.

### (iii) $\text{CsMnCl}_3$

It has been reported<sup>76</sup> that  $\text{CsMnCl}_3$  has space group R3m, however



Table 8. Internal modes of  $\text{MnCl}_4^{2-}$  ion.

$f=Z \cdot \nu_{\text{vib}}$	$\nu_{\text{vib}}$	Molecular Symmetry ( $T_d$ )	correlation	Site Symmetry ( $D_{2d}$ )	correlation	Space Group ( $D_{4h}$ )	
2	1( $\nu_1$ )	$A_1$		$A_1$		$A_{1g}$	1
						$B_{1u}$	1
4	2( $\nu_2$ )	$E$		$A_1$		$A_{1g}$	1
						$B_{1u}$	1
				$B_1$		$B_{1g}$	1
						$A_{1u}$	1
				$E$		$E_g$	1 d
						$E_u$	1 d
6	3( $\nu_3$ )	$T_2$		$B_2$		$B_{2g}$	1
						$A_{2u}$	1
				$E$		$E_g$	1 d
						$E_u$	1 d
6	3( $\nu_4$ )	$T_2$		$B_2$		$B_{2g}$	1
						$A_{2u}$	1
18 modes							18 modes

d: doubly degenerate mode

Table 9. Lattice modes of  $\text{MnCl}_4^{2-}$  ion (Translation).

$f^\gamma = Z \cdot t^\gamma$	$t^\gamma$	$D_{2d}$ Site Symmetry species containing translation ( $\gamma$ )	<u>correlation</u>	$D_{4h}$ Space group
2	$1T_z$	$B_2$	$B_{2g}$	1
			$A_{2u}$	1
4	$2(T_x, T_y)$	$E$	$E_g$	1 d
			$E_u$	1 d
<hr/> 6 modes				<hr/> 6 modes

d: doubly degenerate mode

Table 10. Lattice modes of  $\text{MnCl}_4^{2-}$  ion (Rotation).

$f^\gamma = Z \cdot t^\gamma$	$t^\gamma$	$D_{2d}$ Site Symmetry species containing rotation ( $\gamma$ )	<u>correlation</u>	$D_{4h}$ Space group	
2	$1R_z$	$A_2$	$A_{2g}$	1	
			$B_{2u}$	1	
4	$2(R_x, R_y)$	$E$	$E_g$	1	d
			$E_u$	1	d
<hr/> 6 modes				<hr/> 6 modes	

d: doubly degenerate mode



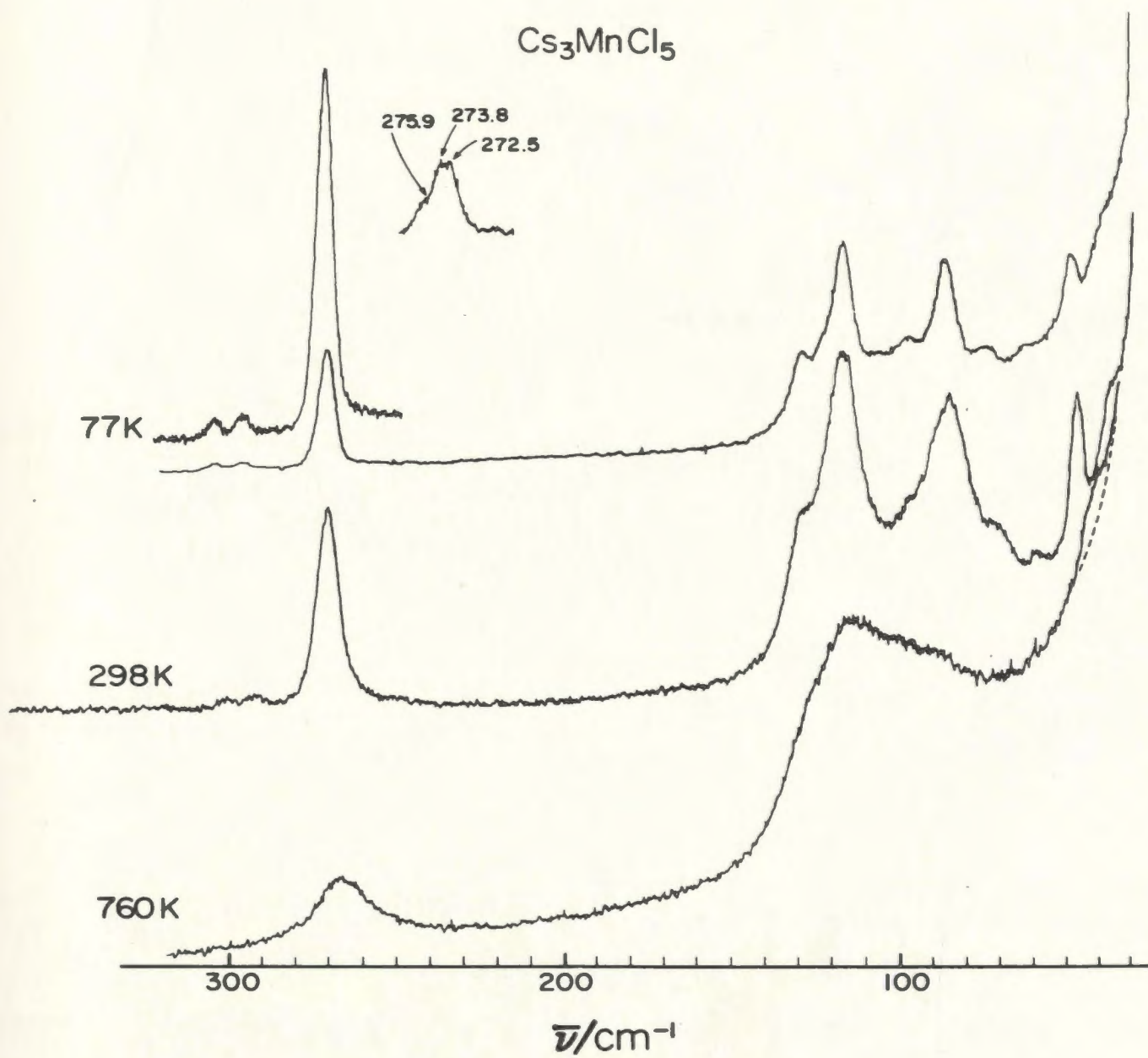
Table 11. Assignments and frequencies in  $\text{cm}^{-1}$  for solid  $\text{Cs}_3\text{MnCl}_5$ .

77 K	Frequency		Assignments
	298 K	760 K	
41 sh,m-w	38 sh,m-w	~41 sh,m	$\left. \begin{matrix} E_g \\ B_{2g} \\ A_{1g} \\ E_g \end{matrix} \right\} \text{Lattice modes}$
51 m-w	49 m		
64 v.w	61 v.w		
77 v.w	72 w		
88 m-w	87 m	~90 w	$\left. \begin{matrix} A_{1g} \\ B_{1g} \end{matrix} \right\} \nu_2$
100 v.w	99 sh, v.w		
119 m	118 m	114 m-s	$\left. \begin{matrix} E_g \\ B_{2g} \end{matrix} \right\} \nu_4$
131 sh,m	130 sh,m		
273 m (5.8) <sup>a</sup>	272 m (8.0)	265 m-w (20)	$A_{1g} \quad \nu_1$
298 v.w	294 v.w		$\left. \begin{matrix} E_g \\ B_{2g} \end{matrix} \right\} \nu_3$
307 v.w	303 v.w		

a: half band width is given in parenthesis

v.w: very weak, w: weak, m: medium, s: strong, sh: shoulder

Figure 5. Raman spectra of solid  $\text{Cs}_3\text{MnCl}_5$  at 77, 298, and 760 K.





neutron diffraction data<sup>53</sup> indicated that  $\text{CsMnCl}_3$  has space group  $R\bar{3}m$ . A recent<sup>52</sup> crystal structure determination on a single crystal of  $\text{CsMnCl}_3$  confirmed that  $\text{CsMnCl}_3$  crystallizes in the centric space group  $R\bar{3}m$  ( $D_{3d}^5$ ) with three formulas per primitive unit cell. The compound consists of  $[\text{Mn}_3\text{Cl}_{12}]$  trimers with each trimer linked to the other trimers by corner sharing, the central manganese atom of a trimer has  $D_{3d}$  site symmetry, and the two terminal manganese atoms of a trimer have  $C_{3v}$  site symmetry. The site symmetries of Cs(1), Cs(2), Cl(1), and Cl(2) atoms are:  $D_{3d}$ ,  $C_{3v}$ ,  $C_{2h}$ ,  $C_s$  respectively. Forty-five modes are predicted from factor group analysis and distributed as follows:

$$\begin{aligned}
 \Gamma_{\text{Cs}(1)} &= A_{2u} + E_u \\
 \Gamma_{\text{Mn}(1)} &= A_{2u} + E_u \\
 \Gamma_{\text{Cs}(2)} &= A_{1g} + E_g + A_{2u} + E_u \\
 \Gamma_{\text{Mn}(2)} &= A_{1g} + E_g + A_{2u} + E_u \\
 \Gamma_{\text{Cl}(1)} &= 4A_{2u} + A_{1u} + 2E_u \\
 \Gamma_{\text{Cl}(2)} &= 4A_{1g} + A_{2g} + 2E_g + 4A_{2u} + A_{1u} + 2E_u \\
 \Gamma_{\text{total}} &= 6A_{1g} + A_{2g} + 4E_g + 12A_{2u} + 2A_{1u} + 8E_u \quad (14) \\
 \Gamma_{\text{acoustic}} &= A_{2u} + E_u
 \end{aligned}$$

$A_{2g}$  and  $A_{1u}$  are inactive, while the u modes are IR active and g modes are Raman active. Ten Raman active modes are predicted as shown from equation (14), but we observed only five Raman peaks. The spectrum of  $\text{CsMnCl}_3$  is shown in figure 6.

Since  $(\text{CH}_3)_4\text{NMnCl}_3$ <sup>54</sup> consists of infinite linear chains composed of manganese atoms bridged by three chlorine atoms  $-\text{MnCl}_3^-$ , and the single crystal Raman of this compound has been reported<sup>55</sup>, the observed

peaks are assigned by analogy with the peaks observed in the spectrum of  $(\text{CH}_3)_4\text{NMnCl}_3$ . Peak positions and assignments are shown in Table 12.

(iv)  $\text{CsMn}_4\text{Cl}_9$

An X-ray study<sup>39</sup> on single crystal of  $\text{CsMn}_4\text{Cl}_9$  indicated that this compound crystallizes in space group  $I4_1/a$  ( $C_{4h}^6$ ) with two formulas per unit cell. The Mn is octahedrally coordinated by Cl atoms, and each  $\text{MnCl}_6$  octahedron is linked to six neighbouring octahedra by sharing five edges and one vertex. The site symmetries are as follows: Cs;  $S_4$ , Mn;  $C_1$ , Cl(1);  $C_1$ , Cl(2);  $C_1$ , Cl(3);  $S_4$ . Eighty-four modes are predicted from factor group analysis and distributed as follows:

$$\begin{aligned}
 \Gamma_{\text{Cs}} &= B_g + E_g + A_u + E_u \\
 \Gamma_{\text{Cl(3)}} &= B_g + E_g + A_u + E_u \\
 \Gamma_{\text{Mn}} &= 2A_g + 2B_g + 4E_g + 2A_u + 2B_u + 4E_u \\
 \Gamma_{\text{Cl(1)}} &= 2A_g + 2B_g + 4E_g + 2A_u + 2B_u + 4E_u \\
 \Gamma_{\text{Cl(2)}} &= 2A_g + 2B_g + 4E_g + 2A_u + 2B_u + 4E_u \\
 \Gamma_{\text{total}} &= 6A_g + 8B_g + 14E_g + 8A_u + 6B_u + 14E_u \\
 \Gamma_{\text{acoustic}} &= A_u + E_u
 \end{aligned} \tag{15}$$

The g modes are Raman active, and u modes are IR active except  $A_u$  is inactive. The Raman spectra of  $\text{CsMn}_4\text{Cl}_9$  and other mixtures in this composition region are shown in figure 6. Tentative assignments and peak frequencies are shown in Table 13.

Table 12. Assignments and peak frequencies in  $\text{cm}^{-1}$  for  $\text{CsMnCl}_3$  and  $(\text{CH}_3)_4\text{NMnCl}_3$ .

$\text{CsMnCl}_3$	Assignments	$(\text{CH}_3)_4\text{NMnCl}_3$	Assignments
48 m-w	$E_g$	88	$E_{2g}$
100 m	$E_g$	118	$E_{1g}$
154 m-w	$E_g$	129	$E_{2g}$
191 w	$E_g$	182	$E_{2g}$
250 w	$A_{1g}$	256	$A_g$

w: weak, m: medium

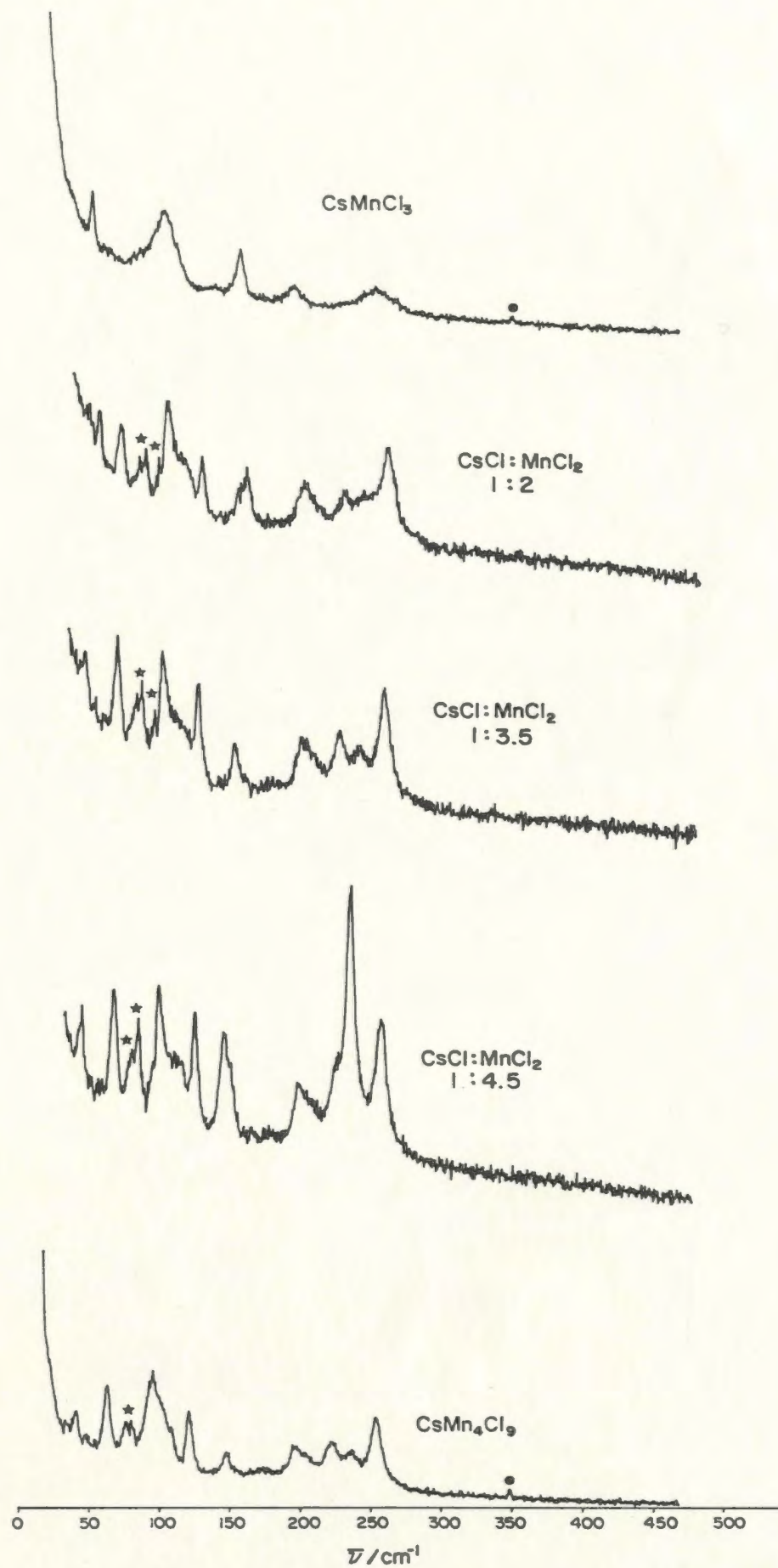


Table 13. Peak frequencies in  $\text{cm}^{-1}$  and assignments for the solid compounds formed in  $\text{CsCl-MnCl}_2$  mixtures.

$\text{CsMn}_4\text{Cl}_9$ I	$\text{CsCl:MnCl}_2$ (1:4.5) I	$\text{CsCl:MnCl}_2$ (1:3.5) I	$\text{CsCl:MnCl}_2$ (1:2) I	Assignments
41 w	42 m-w	42 m-w	41 w	I ( $E_g$ )
50 v.w	50 v.w	50 w	50 m-w	I
63 m	66 m	66 m	65 m	I
96 m	98 m	98 m	99 m	I
102 w,br.				I
108 sh,w	110 w	110 m,br.	108 sh,m-w	I
121 m	124 m	123 m	123 w	I
	144 m		146 sh,w	$E_g$ ( $\text{MnCl}_2$ )
148 w	148 sh,m	149 m-w	154.5 m-w	I
196 w	197 w	200 m-w	196 m-w	I
222 w	226 sh,m-w	224 w	224 w	I
238 v.w	234 s	239 w	238 v.v.w	$A_{1g}$ ( $\text{MnCl}_2$ )
254 m	257 m	256 m	256 m	I ( $A_g$ )

v.w: very weak, w: weak, m: medium, s: strong, sh: shoulder,  
br: broad

Figure 6. Raman spectra of solids formed from the  $\text{CsCl-MnCl}_2$  system. The stars indicate ghost peaks. The dots indicate plasma lines.





### 4.1.3 MnCl<sub>2</sub> - RbCl System

The phase diagram of MnCl<sub>2</sub>-RbCl system<sup>37,38</sup> indicates the presence of three compounds, one congruent compound, RbMnCl<sub>3</sub>; melting point 552°C, and two incongruent compounds, Rb<sub>2</sub>MnCl<sub>4</sub>; melting point 462°C and Rb<sub>3</sub>Mn<sub>2</sub>Cl<sub>7</sub>; melting point 475°C.

#### (i) RbMnCl<sub>3</sub>

An X-ray study<sup>56</sup> on single crystal of RbMnCl<sub>3</sub> indicated that this compound has space group P6<sub>3</sub>/mmc (D<sub>6h</sub><sup>4</sup>) with six formulas per unit cell. The unit cell has six layers of RbCl<sub>3</sub> with the Mn ion situated between the layers and octahedrally coordinated by Cl ions. The site symmetries are as follows: Rb(1); C<sub>2h</sub>, Rb(2); D<sub>3h</sub>, Mn(1); C<sub>2h</sub>, Mn(2); D<sub>3d</sub>, Cl(1); C<sub>1</sub>, Cl(2); C<sub>2</sub>. Ninety modes are predicted from factor group analysis, and distributed as follows:

$$\begin{aligned}
 \Gamma_{\text{Rb}(1)} &= A_{1u} + 2A_{2u} + B_{1u} + 4B_{2u} + E_{1u} + E_{2u} \\
 \Gamma_{\text{Rb}(2)} &= B_{1g} + E_{2g} + A_{2u} + E_{1u} \\
 \Gamma_{\text{Mn}(1)} &= A_{1u} + 2A_{2u} + B_{1u} + 4B_{2u} + E_{1u} + E_{2u} \\
 \Gamma_{\text{Mn}(2)} &= A_{2u} + B_{2u} + E_{1u} + E_{2u} \\
 \Gamma_{\text{Cl}(1)} &= 4A_{1g} + A_{2g} + B_{1g} + 4E_{1g} + 5E_{2g} + A_{2u} + B_{1u} + 4E_{1u} + E_{2u} \\
 \Gamma_{\text{Cl}(2)} &= A_{1g} + 4A_{2g} + 2B_{1g} + 2E_{1g} + 2E_{2g} + B_{1u} + E_{1u} \\
 \Gamma_{\text{total}} &= 5A_{1g} + 5A_{2g} + 4B_{1g} + 6E_{1g} + 8E_{2g} + 2A_{1u} + 7A_{2u} + 4B_{1u} + 9B_{2u} + 9E_{1u} + 4E_{2u} \quad (16) \\
 \Gamma_{\text{acoustic}} &= A_{2u} + E_{1u}
 \end{aligned}$$

$A_{2g}$  and  $B_{1g}$  are inactive while  $A_{1g}$ ,  $E_{1g}$ , and  $E_{2g}$  are Raman active, and the u modes are IR active except  $B_{1u}$  and  $B_{2u}$  which are inactive.

The Raman spectrum of  $RbMnCl_3$  is shown in figure 7. The assignments have been made by analogy with the Raman spectrum of  $RbMnCl_3$  crystal<sup>70</sup> at 50 K. Assignments and peak positions are shown in Table 14.

(ii)  $Rb_2MnCl_4$

An X-ray diffraction pattern<sup>57</sup> and neutron diffraction data<sup>45</sup> of  $Rb_2MnCl_4$  showed that this compound crystallizes in space group  $I4/mmm$  ( $D_{4h}^{17}$ ) with one formula per unit cell. The compound is isostructural with  $K_2MgCl_4$ <sup>42</sup>. The Mn atom is octahedrally coordinated by Cl atoms, and the site symmetries are as follows: Rb;  $C_{4v}$ , Mn;  $D_{4h}$ , Cl(1);  $D_{2h}$ , Cl(2);  $C_{4v}$ . Twenty-one modes are predicted from factor group analysis, and distributed as follows:

$$\begin{aligned}
 \Gamma_{Rb} &= A_{1g} + E_g + A_{2u} + E_u \\
 \Gamma_{Mn} &= A_{2u} + E_u \\
 \Gamma_{Cl(1)} &= A_{2u} + B_{2u} + 2E_u \\
 \Gamma_{Cl(2)} &= A_{1g} + E_g + A_{2u} + E_u \\
 \Gamma_{total} &= 2A_{1g} + 2E_g + 4A_{2u} + B_{2u} + 5E_u \\
 \Gamma_{acoustic} &= A_{2u} + E_u
 \end{aligned} \tag{17}$$

All g modes are Raman active, and the u modes are IR active except  $B_{2u}$  is inactive. Four modes are predicted in the Raman spectrum, two peaks are observed, and the other two peaks are not detected in the spectrum because of the presence of a ghost in the range  $80-120 \text{ cm}^{-1}$ . The assignments are made by analogy with the spectrum of single crystal

Table 14. Assignments and frequencies in  $\text{cm}^{-1}$  for solid  $\text{RbMnCl}_3$ .

$\text{RbMnCl}_3$ Solid at room temperature	$\text{RbMnCl}_3^{70}$ Crystal at 50 K	Assignments
	19	$A_{1g}$
	28	$E_{1g}$
	44	$E_{2g}$
52 sh,m	53	$E_{2g}$
	74	$E_{2g}$
	130	$E_{1g}$
	135	$A_{1g}$
152 w	150	$E_{2g}$
171.5 v.w	170	$A_{1g}$
	180	$E_{2g}$
	218	$E_{2g}$
258 v.w	257	$A_{1g}$

v.w: very weak, w: weak, m: medium, sh: shoulder



$\text{Rb}_2\text{MnCl}_4$ <sup>59,60</sup>. The spectra of  $\text{Rb}_2\text{MnCl}_4$ ,  $\text{RbCl}:\text{MnCl}_2$  (3:1), and  $\text{RbCl}:\text{MnCl}_2$  (4:1) are shown in figure 7, and peak frequencies and assignments are shown in Table 15.

(iii)  $\text{Rb}_3\text{Mn}_2\text{Cl}_7$

The X-ray diffraction pattern<sup>43,57</sup> of  $\text{Rb}_3\text{Mn}_2\text{Cl}_7$  indicated that this incongruent melting compound is isostructural with  $\text{Sr}_3\text{Ti}_2\text{O}_7$ <sup>61</sup>, and has space group  $I4/mmm$  ( $D_{4h}^{17}$ ) with two formulas per unit cell. The site symmetries are as follows: Mn;  $C_{4v}$ , Rb(1);  $D_{4h}$ , Rb(2);  $C_{4v}$ , Cl(1);  $D_{4h}$ , Cl(2);  $C_{2v}$ , Cl(3);  $C_{4v}$ . Factor group analysis predicted seventy-two modes distributed as follows:

$$\begin{aligned}
 \Gamma_{\text{Cl}(1)} &= 2A_{2u} + 2E_u \\
 \Gamma_{\text{Rb}(1)} &= 2A_{2u} + 2E_u \\
 \Gamma_{\text{Rb}(2)} &= 2A_{1g} + 2E_g + 2A_{2u} + 2E_u \\
 \Gamma_{\text{Mn}} &= 2A_{1g} + 2E_g + 2A_{2u} + 2E_u \\
 \Gamma_{\text{Cl}(3)} &= 2A_{1g} + 2E_g + 2A_{2u} + 2E_u \\
 \Gamma_{\text{Cl}(2)} &= 2A_{1g} + 2B_{1g} + 4E_g + 2A_{2u} + 2B_{2u} + 4E_u \\
 \Gamma_{\text{total}} &= 8A_{1g} + 2B_{1g} + 10E_g + 12A_{2u} + 2B_{2u} + 14E_u \\
 \Gamma_{\text{acoustic}} &= A_{2u} + E_u
 \end{aligned} \tag{18}$$

All g modes are Raman active, while  $A_{2u}$  and  $E_u$  modes are IR active and  $B_{2u}$  is inactive. The Raman spectrum of  $\text{Rb}_3\text{Mn}_2\text{Cl}_7$  is shown in figure 7. The spectrum seems to be similar to the spectra of  $\text{RbMnCl}_3$  and  $\text{Rb}_2\text{MnCl}_4$ . Assignments have been made by analogy with  $\text{RbMnCl}_3$  and  $\text{Rb}_2\text{MnCl}_4$ . Recently<sup>60</sup> six Raman peaks were observed without assignments for  $\text{Rb}_3\text{Mn}_2\text{Cl}_7$ . Tentative assignments and frequencies in  $\text{cm}^{-1}$  are shown in Table 16.

Table 15. Peak frequencies in  $\text{cm}^{-1}$  and assignments for the solid compounds formed in  $\text{RbCl-MnCl}_2$  mixtures.

$\text{Rb}_2\text{MnCl}_4$ I	$\text{RbCl:MnCl}_2$ (3:1) I	$\text{RbCl:MnCl}_2$ (4:1) I	$\text{Rb}_2\text{MnCl}_4^{59}$ at 300 K	Assignments
52 s-m	52 m	52 m	52	$E_g(\text{I})$
			89.5	$A_{1g}$
			97.5	$E_g$
200 m-w	200 m-w	200 m-w	201	$A_{1g}(\text{I})$

w: weak, m: medium, s: strong

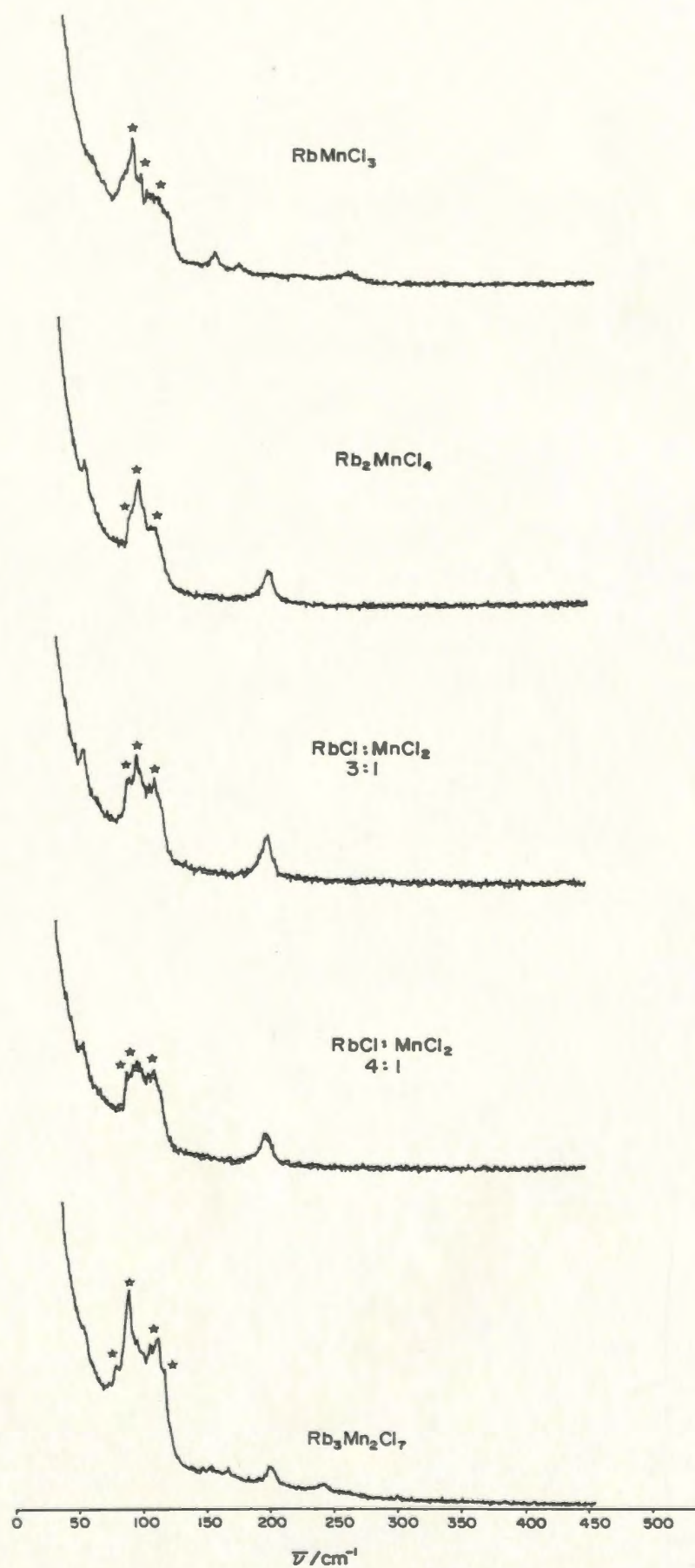
Table 16. Assignments and peak frequencies in  $\text{cm}^{-1}$  for solid  $\text{Rb}_3\text{Mn}_2\text{Cl}_7$ .

$\text{Rb}_3\text{Mn}_2\text{Cl}_7$	$\text{Rb}_3\text{Mn}_2\text{Cl}_7^{60}$	Assignments
	36	
51 sh,w		$\begin{cases} E_{2g} (\text{RbMnCl}_3) \\ E_g (\text{Rb}_2\text{MnCl}_4) \end{cases}$
	78	
	98	
	115	
148 v.w		$E_g (\text{MnCl}_2)$
156 v.w		$E_{2g} (\text{RbMnCl}_3)$
166 v.w.	166	$A_{1g} (\text{RbMnCl}_3)$
200 w		$A_{1g} (\text{Rb}_2\text{MnCl}_4)$
240 v.w	242	$A_{1g} (\text{MnCl}_2)$

v.w: very weak, w: weak, sh: shoulder



Figure 7. Raman spectra of solids formed from the  $\text{RbCl-MnCl}_2$  system. The stars indicate ghost peaks.



#### 4.1.4 $\text{MnCl}_2\text{-KCl}$ System

The phase diagram of  $\text{MnCl}_2\text{-KCl}$  system<sup>37,57</sup> indicated the presence of three double salts, one congruent compound,  $\text{KMnCl}_3$ ; melting point  $490^\circ\text{C}$ , and two incongruent compounds,  $\text{K}_3\text{Mn}_2\text{Cl}_7$ ; melting point  $437^\circ\text{C}$  and  $\text{K}_4\text{MnCl}_6$ ; melting point  $448^\circ\text{C}$ . Kuzmenko et. al<sup>58</sup> reported that there are three coordination compounds for  $\text{KCl-MnCl}_2$  system, one congruent compound  $\text{KMnCl}_3$ , and two incongruent compounds  $\text{K}_3\text{Mn}_2\text{Cl}_7$  and  $\text{K}_2\text{MnCl}_4$ .

$\text{K}_3\text{Mn}_2\text{Cl}_7$ <sup>43,57</sup> is isostructural with  $\text{Rb}_3\text{Mn}_2\text{Cl}_7$ <sup>43,57</sup>, and the number of modes predicted from factor group analysis are given by equation 18.  $\text{KMnCl}_3$ <sup>43</sup> is isostructural with  $\text{KMgCl}_3$ <sup>77</sup> with space group  $\text{Pnma}$  ( $D_{2h}^{16}$ ) and four formulas per unit cell. Seifert<sup>43</sup> reported a high temperature phase which we have not studied. The site symmetries are as follows: K;  $C_s$ , Mn;  $C_i$ , Cl(1);  $C_s$ , Cl(2);  $C_1$ . The number of modes predicted from factor group analysis are distributed as follows:

$$\begin{aligned}
 \Gamma_{\text{Mn}} &= 3A_u + 3B_{1u} + 3B_{2u} + 3B_{3u} \\
 \Gamma_{\text{K}} &= 2A_g + 2B_{1g} + B_{2g} + B_{3g} + A_u + B_{1u} + 2B_{2u} + 2B_{3u} \\
 \Gamma_{\text{Cl(1)}} &= 2A_g + 2B_{1g} + B_{2g} + B_{3g} + A_u + B_{1u} + 2B_{2u} + 2B_{3u} \\
 \Gamma_{\text{Cl(2)}} &= 3A_g + 3B_{1g} + 3B_{2g} + 3B_{3g} + 3A_u + 3B_{1u} + 3B_{2u} + 3B_{3u} \\
 \Gamma_{\text{total}} &= 7A_g + 7B_{1g} + 5B_{2g} + 5B_{3g} + 8A_u + 8B_{1u} + 10B_{2u} + 10B_{3u} \quad (19) \\
 \Gamma_{\text{acoustic}} &= B_{1u} + B_{2u} + B_{3u}
 \end{aligned}$$

$A_u$  is inactive, and u modes are IR active while the g modes are Raman active.

$\text{K}_4\text{MnCl}_6$ <sup>62,63</sup> has space group  $\text{R}\bar{3}\text{c}$  ( $D_{3d}^6$ ) with two formulas per unit cell. The site symmetries are as follows: K(1),  $C_{3i}$ , K(2);  $C_i$ , Mn;  $D_3$ , Cl;  $C_1$ . The number of modes predicted from factor group analysis are distributed as follows:



$$\begin{aligned}
 \Gamma_{\text{Mn}} &= A_{2g} + E_g + A_{2u} + E_u \\
 \Gamma_{\text{K}(1)} &= A_{1u} + A_{2u} + 2E_u \\
 \Gamma_{\text{K}(2)} &= 4A_{1u} + 4A_{2u} + 5E_u \\
 \Gamma_{\text{Cl}} &= 3A_{1g} + 3A_{2g} + 10E_g + 3A_{1u} + 3A_{2u} + 2E_u \\
 \Gamma_{\text{total}} &= 3A_{1g} + 4A_{2g} + 11E_g + 8A_{1u} + 9A_{2u} + 10E_u \\
 \Gamma_{\text{acoustic}} &= A_{2u} + E_u
 \end{aligned} \tag{20}$$

$A_{2g}$  and  $A_{1u}$  are inactive, while  $A_{1g}$  and  $E_g$  are Raman active and  $A_{2u}$  and  $E_u$  are IR active.

The Raman spectra for  $\text{KMnCl}_3$ ,  $\text{K}_3\text{Mn}_2\text{Cl}_7$ ,  $\text{K}_4\text{MnCl}_6$ ,  $\text{KCl}:\text{MnCl}_2$  (2:1) and  $\text{KCl}:\text{MnCl}_2$  (3:1) are shown in figure 8. Assignments and peak frequencies are shown in Table 17. The Raman spectrum can not distinguish whether the compound is  $\text{K}_2\text{MnCl}_4$  or  $\text{K}_4\text{MnCl}_6$ .

#### 4.1.5 $\text{MnCl}_2$ -NaCl System

The phase diagram study<sup>43,64</sup> indicated the presence of five incongruent compounds,  $\text{NaMnCl}_3$ ; melting point  $424^\circ\text{C}$ ,  $\text{Na}_2\text{MnCl}_4$ ; melting point  $442^\circ\text{C}$ ,  $\text{Na}_2\text{Mn}_3\text{Cl}_8$ ; melting point  $413^\circ\text{C}$ ,  $\text{NaMn}_4\text{Cl}_9$ ; melting point  $451^\circ\text{C}$ ,  $\text{Na}_6\text{MnCl}_8$ ; melting point  $459^\circ\text{C}$ .

An X-ray study<sup>65</sup> on single crystal of  $\text{NaMnCl}_3$  indicated that  $\text{NaMnCl}_3$  crystallizes in space group  $R\bar{3}$  ( $C_{3i}^2$ ) with two formulas per unit cell. It is isomorphous with  $\text{FeTiO}_3$ <sup>66</sup>. The site symmetries are as follows: Na;  $C_3$ , Mn;  $C_3$ , Cl;  $C_1$ . Thirty modes are predicted from factor group analysis, and distributed as follows:

$$\begin{aligned}
 \Gamma_{\text{Na}} &= A_g + E_g + A_u + E_u \\
 \Gamma_{\text{Mn}} &= A_g + E_g + A_u + E_u \\
 \Gamma_{\text{Cl}} &= 3A_g + 3E_g + 3A_u + 3E_u \\
 \Gamma_{\text{total}} &= 5A_g + 5E_g + 5A_u + 5E_u \\
 \Gamma_{\text{acoustic}} &= A_u + E_u
 \end{aligned} \tag{21}$$

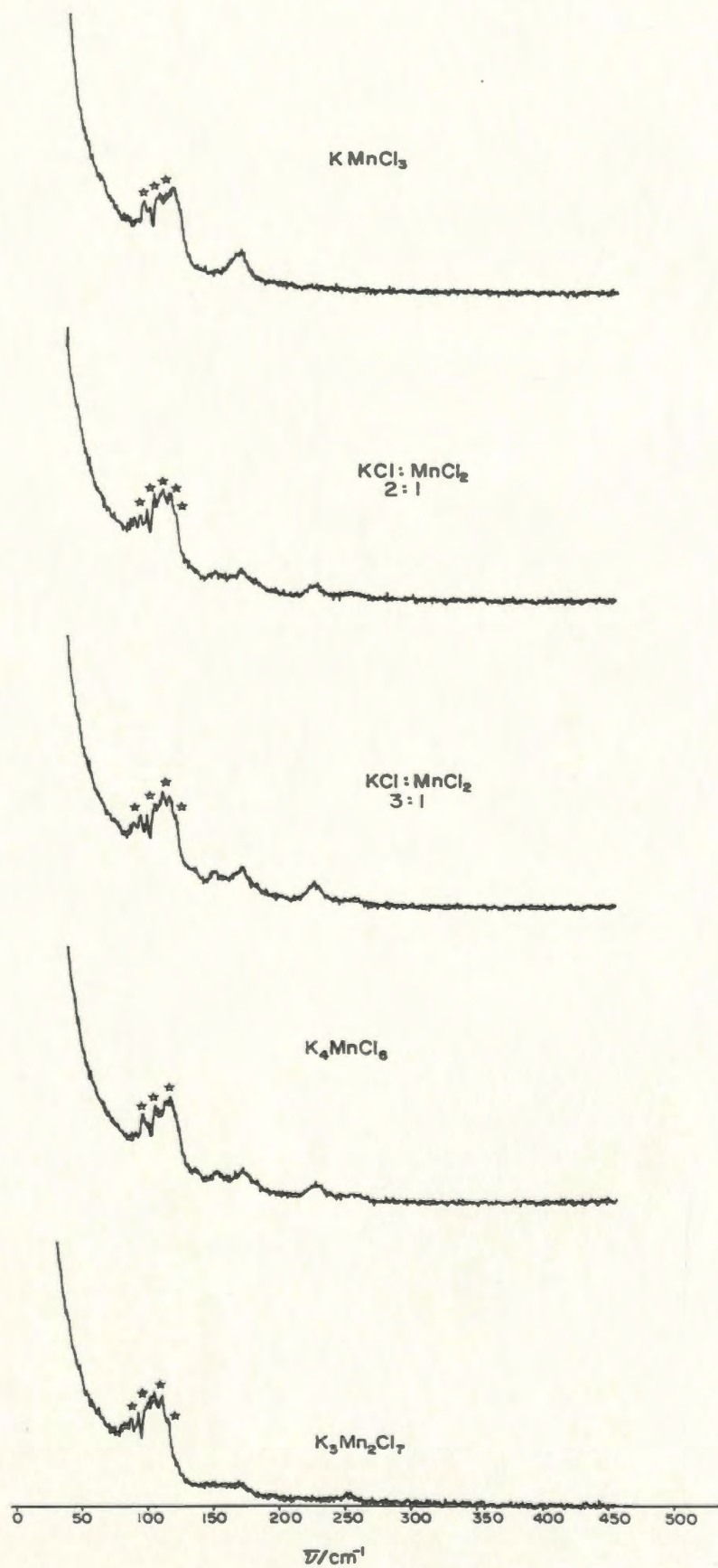
Table 17. Assignments and peak frequencies in  $\text{cm}^{-1}$  for the solid compounds  
formed in  $\text{KCl-MnCl}_2$  system.

$\text{KMnCl}_3$ I	$\text{K}_3\text{Mn}_2\text{Cl}_7$ II	$\text{K}_4\text{MnCl}_6$ III	$\text{KCl:MnCl}_2$ (2:1) III	$\text{KCl:MnCl}_2$ (3:1) III	Assignments
		130 v.w	128 v.w	130 v.w	III
		146 v.w	146 v.w	144 v.w	$E_g (\text{MnCl}_2)$
162 w					I
		165 w	164 w	166 w	III
	174 v.w				II
		222 w	222 w	222 w	III
	251 v.w				II
		250 v.w	250 v.w	252 v.w	III

v.w: very weak, w: weak

Figure 8. Raman spectra of solids formed from the  $\text{KCl-MnCl}_2$  system. The stars indicate ghost peaks.





All the g modes are Raman active, and all the u modes are IR active.

An X-ray study<sup>67</sup> on single crystal of  $\text{Na}_2\text{MnCl}_4$  indicated that  $\text{Na}_2\text{MnCl}_4$  has space group  $\text{Pbam}$  ( $D_{2h}^9$ ) with two formulas per unit cell. The site symmetries are as follows: Mn;  $C_{2h}$ , Na;  $C_s$ , Cl(1);  $C_s$ , Cl(2);  $C_s$ .

Forty-two modes are predicted as follows:

$$\begin{aligned}
 \Gamma_{\text{Mn}} &= 2B_{2u} + 2B_{3u} + A_u + B_{1u} \\
 \Gamma_{\text{Na}} &= 2A_g + 2B_{1g} + B_{2g} + B_{3g} + 2B_{2u} + 2B_{3u} + A_u + B_{1u} \\
 \Gamma_{\text{Cl(1)}} &= 2A_g + 2B_{1g} + B_{2g} + B_{3g} + 2B_{2u} + 2B_{3u} + A_u + B_{1u} \\
 \Gamma_{\text{Cl(2)}} &= 2A_g + 2B_{1g} + B_{2g} + B_{3g} + 2B_{2u} + 2B_{3u} + A_u + B_{1u} \\
 \Gamma_{\text{total}} &= 6A_g + 6B_{1g} + 3B_{2g} + 3B_{3g} + 8B_{2u} + 8B_{3u} + 4A_u + 4B_{1u} \quad (22) \\
 \Gamma_{\text{acoustic}} &= B_{2u} + B_{3u} + B_{1u}
 \end{aligned}$$

$A_u$  is inactive, all the u modes are IR active, while the g modes are Raman active.

An X-ray study<sup>68</sup> on powder samples of  $\text{Na}_6\text{MnCl}_8$  and  $\text{Na}_2\text{Mn}_3\text{Cl}_8$  have been made. The results indicated that  $\text{Na}_2\text{Mn}_3\text{Cl}_8$  has space group  $R\bar{3}m$  ( $D_{3d}^5$ ) with one formula per unit cell, and the site symmetries are as follows: Na;  $C_{3v}$ , Mn;  $C_{2h}$ , Cl(1);  $C_{3v}$ , Cl(2);  $C_s$ .  $\text{Na}_6\text{MnCl}_8$  has space group  $\text{Fm}\bar{3}m$  ( $O_h^5$ ), with one formula per unit cell, the site symmetries are as follows:

Na;  $D_{2h}$ , Mn;  $O_h$ , Cl(1);  $T_d$ , Cl(2);  $C_{4v}$ . The number of modes predicted from factor group analysis for  $\text{Na}_2\text{Mn}_3\text{Cl}_8$  are as follows:

$$\begin{aligned}
 \Gamma_{\text{Na}} &= A_{1g} + E_g + A_{2u} + E_u \\
 \Gamma_{\text{Cl(1)}} &= A_{1g} + E_g + A_{2u} + E_u \\
 \Gamma_{\text{Mn}} &= 4A_{2u} + A_{1u} + 2E_u
 \end{aligned}$$

$$\begin{aligned}
 \Gamma_{Cl(2)} &= 4A_{1g} + A_{2g} + 2E_g + 4A_{2u} + A_{1u} + 2E_u \\
 \Gamma_{total} &= 6A_{1g} + A_{2g} + 4E_g + 10A_{2u} + 2A_{1u} + 6E_u \\
 \Gamma_{acoustic} &= A_{2u} + E_u
 \end{aligned} \tag{23}$$

$A_{2g}$  and  $A_{1u}$  are inactive, while  $A_{1g}$  and  $E_g$  are Raman active and  $A_{2u}$  and  $E_u$  are IR active.

Forty-five modes are predicted from factor group analysis for  $Na_6MnCl_8$ , and distributed as follows:

$$\begin{aligned}
 \Gamma_{Mn} &= T_{1u} \\
 \Gamma_{Cl(1)} &= 2T_{1u} \\
 \Gamma_{Na} &= 6T_{1u} \\
 \Gamma_{Cl(2)} &= A_{1g} + E_g + 2T_{2g} + 3T_{1u} \\
 \Gamma_{total} &= A_{1g} + E_g + 2T_{2g} + 12T_{1u} \\
 \Gamma_{acoustic} &= T_{1u}
 \end{aligned} \tag{24}$$

All g modes are Raman active and  $T_{1u}$  is IR active.

The crystal structure of  $NaMn_4Cl_9$  has not yet been determined. Two peaks were observed at 232 and 142  $cm^{-1}$  for  $NaMn_4Cl_9$ , and these two peaks are most probably due to  $MnCl_2$ . The failure to detect peaks that can be assigned to a  $NaMn_4Cl_9$  compound suggest that the compound does not exist or that the Raman features are too weak to detect. The spectrum of  $Na_6MnCl_8$  is assigned by analogy with the Raman spectrum<sup>69</sup> of the Suzuki phase ( $6NaCl:MnCl_2$ ). The Raman spectra of  $NaMnCl_3$ ,  $Na_2MnCl_4$ ,  $Na_2Mn_3Cl_8$ ,  $NaMn_4Cl_9$ , and  $Na_6MnCl_8$  are shown in figure 9. Assignments and peak frequencies are shown in Table 18.

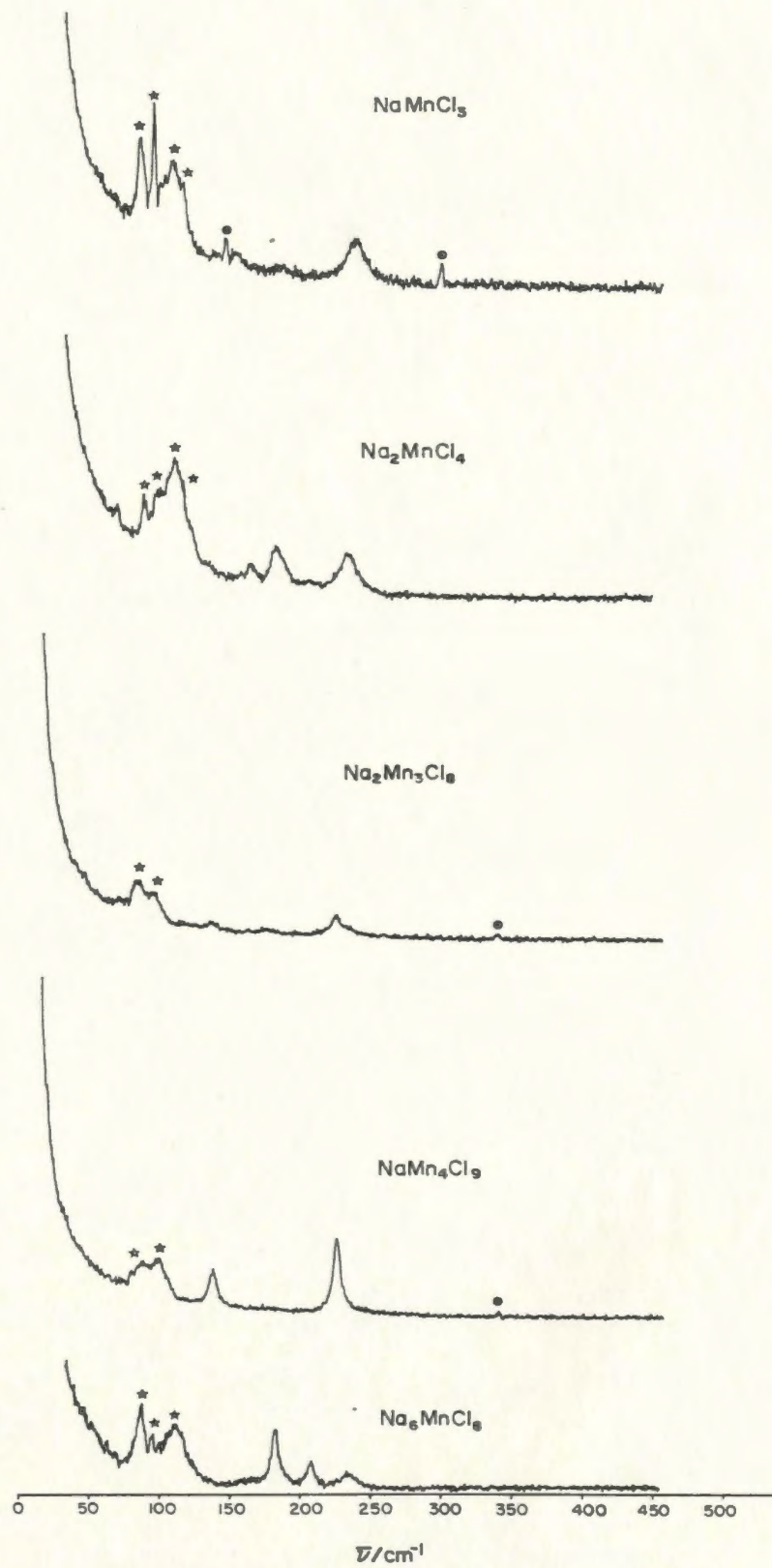


Table 18. Assignments and frequencies in  $\text{cm}^{-1}$  for the solid compounds formed in  $\text{MnCl}_2\text{-NaCl}$  system.

$\text{NaMnCl}_3$ I	$\text{Na}_2\text{MnCl}_4$ II	$\text{Na}_2\text{Mn}_3\text{Cl}_8$ III	$\text{NaMn}_4\text{Cl}_9$ IV	$\text{Na}_6\text{MnCl}_8$ V	Suzuki phase <sup>69</sup>	Assignments
	68 w					II
					123	$T_{2g}$
		123 v.w				III
	132 v.w					II
139 v.w						I
		142 v.w	142 m-w			$E_g (\text{MnCl}_2)$
151 v.w						I
	166 v.w					II
		182 v.w				III
				182 m	180	$T_{2g}$
	183 w					II
185 v.w						I
				208 w	206	$A_{1g}$
236 w	234 w	232 w	232 m	235 w		$A_{1g} (\text{MnCl}_2)$

v.w: very weak, w: weak, m: medium

Figure 9. Raman spectra of solids formed from the  $\text{NaCl-MnCl}_2$  system. The stars indicate ghost peaks. The dots indicate plasma lines.





#### 4.1.6 MnCl<sub>2</sub>-LiCl System

It has been reported<sup>72</sup> that, the MnCl<sub>2</sub>-LiCl system forms a solid solution over the whole composition range. However, the Raman spectrum of the LiCl:MnCl<sub>2</sub> (1:1) mixture indicates that this mixture has separated into crystalline MnCl<sub>2</sub> and LiCl, and it may contain a small concentration of Li<sub>2</sub>MnCl<sub>4</sub>. A neutron diffraction study<sup>73</sup> concluded that Li<sub>2</sub>MnCl<sub>4</sub> has space group Fd3m ( $O_h^7$ ) with two formulas per unit cell, and the site symmetries of the atoms are as follows: Li(1); D<sub>3d</sub>, Li(2); Td, Mn; D<sub>3d</sub>, Cl; C<sub>3v</sub>.

Forty-two modes are predicted from factor group analysis and distributed as follows:

$$\begin{aligned}
 \Gamma_{\text{Li}(2)} &= T_{2g} + T_{1u} \\
 \Gamma_{\text{Li}(1)} &= A_{2u} + E_u + T_{1u} \\
 \Gamma_{\text{Mn}} &= A_{2u} + E_u + T_{1u} \\
 \Gamma_{\text{Cl}} &= 2A_{1g} + 2E_g + 2T_{2g} + 2A_{2u} + 2E_u + 2T_{1u} \\
 \Gamma_{\text{total}} &= 2A_{1g} + 2E_g + 3T_{2g} + 4A_{2u} + 4E_u + 5T_{1u} \\
 \Gamma_{\text{acoustic}} &= T_{1u}
 \end{aligned} \tag{25}$$

All the g modes are Raman active and T<sub>1u</sub> is IR active. A<sub>2u</sub> and E<sub>u</sub> are inactive. The Raman spectra in the solid state of LiCl:MnCl<sub>2</sub> (1:1), Li<sub>2</sub>MnCl<sub>4</sub>, and LiCl:MnCl<sub>2</sub> (3:1) are shown in figure 10, and the peak frequencies in cm<sup>-1</sup> and assignments are shown in Table 19.

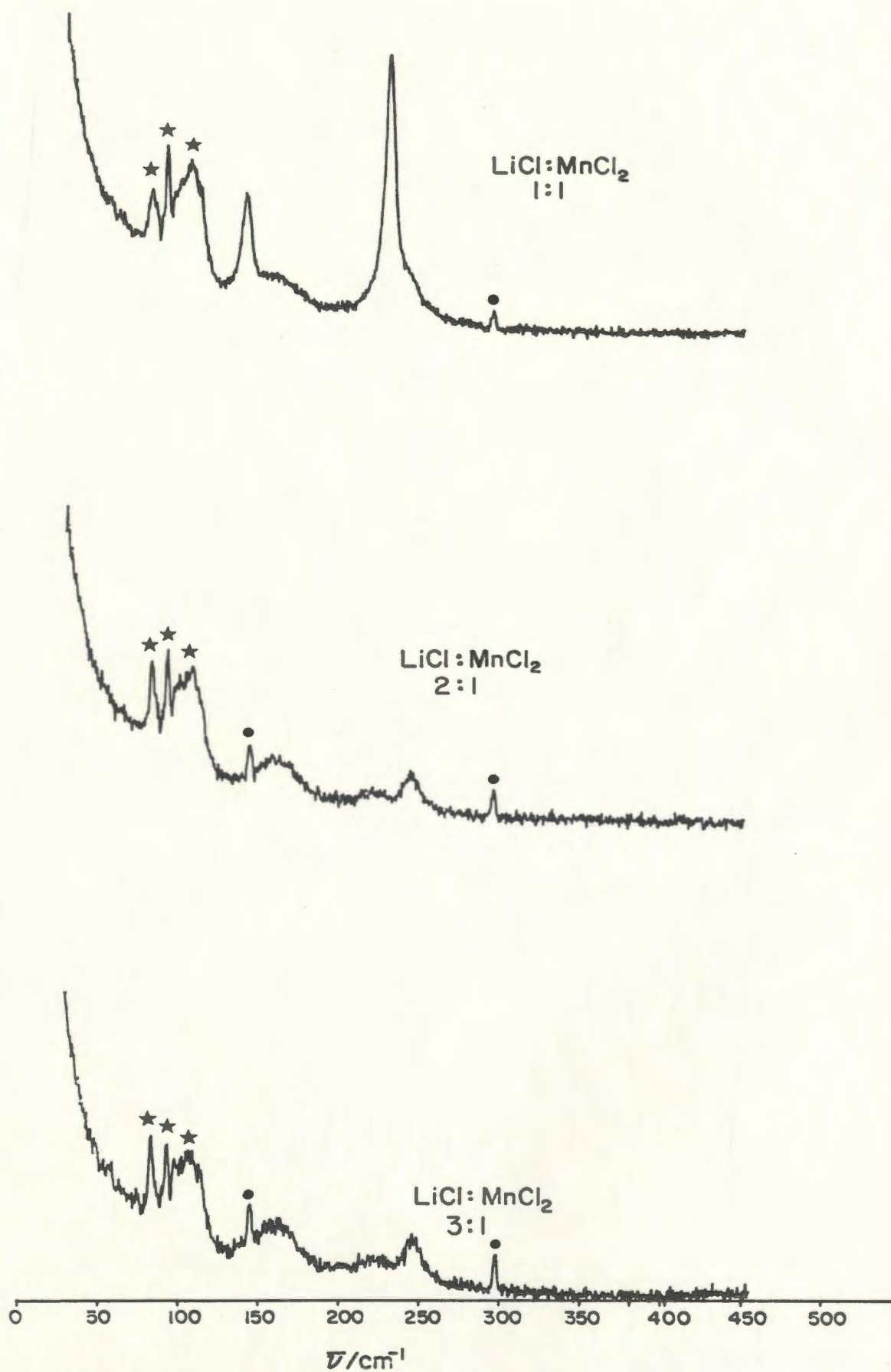
Table 19. Peak frequencies in  $\text{cm}^{-1}$  and assignments for the solid compounds formed in  $\text{LiCl-MnCl}_2$  system.

$\text{LiCl:MnCl}_2$ (1:1) I	$\text{Li}_2\text{MnCl}_4$ II	$\text{Li}_2\text{MnCl}_4^{74}$ II	$\text{LiCl:MnCl}_2$ (3:1) II	Assignments
		70		II
		120		II
143 m				$E_g (\text{MnCl}_2)$
166 sh,w	164 w	163	162 w	II
	222 v.w	227	225 v.w	II
233 s				$A_{1g} (\text{MnCl}_2)$
247 sh,w	246 w	248	246 w	II

v.w: very weak, w: weak, m: medium, s: strong, sh: shoulder

Figure 10. Raman spectra of solids formed from the  $\text{LiCl-MnCl}_2$  system. The stars indicate ghost peaks. The dots indicate plasma lines.





## 4.2 Raman Studies of $\text{MnCl}_2 \cdot n\text{ACl}$ : Molten State

### 4.2.1 $\text{MnCl}_2$ , and $\text{MnCl}_2\text{-CsCl}$ Melts

The Raman spectra of  $\text{MnCl}_2$ ,  $\text{Cs}_2\text{MnCl}_4$ ,  $\text{Cs}_3\text{MnCl}_5$ ,  $\text{CsMnCl}_3$ , and  $\text{CsMn}_4\text{Cl}_9$  are shown in figures 11, 12, 13, 14, and 15 respectively. Two sets of spectra are shown for each melt, one in which the observed intensity,  $I_{(\bar{\nu})}^{\text{obs}}$  is plotted as a function of frequency ( $\bar{\nu}$  in  $\text{cm}^{-1}$ ) and which is what the Raman spectrometer measures directly, and the other which is the corrected intensity  $R_2(\bar{\nu})$  and is directly related to the density of vibrational states as discussed previously.

The spectra can be assigned to modes expected from a tetrahedral  $\text{MnCl}_4^{2-}$  species. A totally symmetric stretching mode ( $\nu_1$ ) is observed in each spectrum in the range  $160\text{-}350\text{ cm}^{-1}$ . The  $\nu_2$  and  $\nu_4$  modes are observed as an overlapped peaks in the region  $75\text{-}135\text{ cm}^{-1}$ . The anti-symmetric stretching mode  $\nu_3$  should appear around  $\sim 300\text{ cm}^{-1}$  but is too weak to be observed or is probably obscured under the polarized peak centered at  $\sim 250\text{ cm}^{-1}$ . A peak due to  $\nu_3$  was observed<sup>50</sup> as strong band at  $284\text{ cm}^{-1}$  in the IR spectrum of solid  $(\text{Et}_4\text{N})_2\text{MnCl}_4$ .

The spectra of melts of composition  $\text{MnCl}_2 \cdot n\text{CsCl}$  ( $n \geq 2$ ) strongly indicate the presence of an isolated tetrahedral  $\text{MnCl}_4^{2-}$  ion, but for melts of composition  $\text{MnCl}_2 \cdot n\text{CsCl}$  ( $n < 2$ ) tetrahedral  $\text{MnCl}_4^{2-}$  ions with corner shared Cl are suggested. A previous Raman study<sup>19</sup> of  $\text{MnCl}_2 \cdot \text{KCl}$  melts suggested that  $\text{MnCl}_2$  melt has  $(\text{MnCl}_2)_n$  species in which  $\text{Mn}^{2+}$  ion is octahedrally coordinated by six  $\text{Cl}^-$  ions and each  $\text{Cl}^-$  ion is shared by  $\text{Mn}^{2+}$  ions, also the existence of a small amount of  $\text{MnCl}_4^{2-}$  was proposed. However, tetrahedral coordination of Cl ions around a Mn ion through corner sharing was proposed<sup>29</sup> from molten  $\text{MnCl}_2$  by x-ray diffraction. In the present study one broad polarized peak was observed

for  $\text{MnCl}_2$  melt and melts of higher  $\text{MnCl}_2$  concentration and this peak was attributed to Mn-Cl stretching vibration of tetrahedral  $\text{MnCl}_4^{2-}$  ion.  $\text{MnCl}_2$  melt and melts of higher  $\text{MnCl}_2$  content appear to have a rapid equilibrium of ions with most Mn retaining a tetrahedral coordination but octahedral coordination may be present to a small extent.



The existence of short lived  $\text{Mn}_2\text{Cl}_7^{3-}$  ions seem probable and the visible spectra of the  $\text{MnCl}_2$  melt and melt mixtures of high  $\text{MnCl}_2$  content suggest the presence of small amount of octahedrally coordinated  $\text{Mn}^{2+}$ , see figures 117, 118, 119 and 120.

It has been reported that the half band width of the totally symmetric mode of  $\text{MnCl}_2$ -KCl melts<sup>19</sup> increased with increased  $\text{MnCl}_2$  content. The present results confirmed this increment in the half band width upon increasing  $\text{MnCl}_2$  concentration for the  $\text{CsCl}$ - $\text{MnCl}_2$  system, see Table 20.

The Raman spectra for solid  $\text{Cs}_2\text{MnCl}_4$  and  $\text{Cs}_3\text{MnCl}_5$  are recorded at several temperatures up to their melting points. The results for the totally symmetric mode ( $\nu_1$ ) for  $\text{Cs}_2\text{MnCl}_4$  and  $\text{Cs}_3\text{MnCl}_5$  are shown in figures 16 and 17. The band position moved to lower values as the temperature was increased, while the half band width increased with increased temperature.



Table 20. Summary of results of curve resolution analysis for  $\text{MnCl}_2$  and  $\text{MnCl}_2$ -CsCl Melts.

Compound	Frequency ( $\text{cm}^{-1}$ )	Intensity	Half band width ( $\text{cm}^{-1}$ )	Function
$\text{Cs}_3\text{MnCl}_5$	255.7	904	35.3	L
$\text{Cs}_2\text{MnCl}_4$	256.7	914	39.9	L
$\text{CsMnCl}_3$	262.7 <sup>a</sup>	817 <sup>a</sup>	81.8 <sup>a</sup>	G * L
	262.3 <sup>a</sup>	859 <sup>a</sup>	78.9 <sup>a</sup>	L
$\text{CsMn}_4\text{Cl}_9$	245.5	683	114.5	G * L
$\text{MnCl}_2$	235.3	794	135.4	G * L

G: Gaussian, L: Lorentzian

<sup>a</sup> Comparison of the fits for G \* L and L models indicates the insensitivity to chosen function.

Figure 11. Raman spectra of molten  $\text{MnCl}_2$  at 942 K,  $I_{||}$   
and  $I_{\perp}$ .

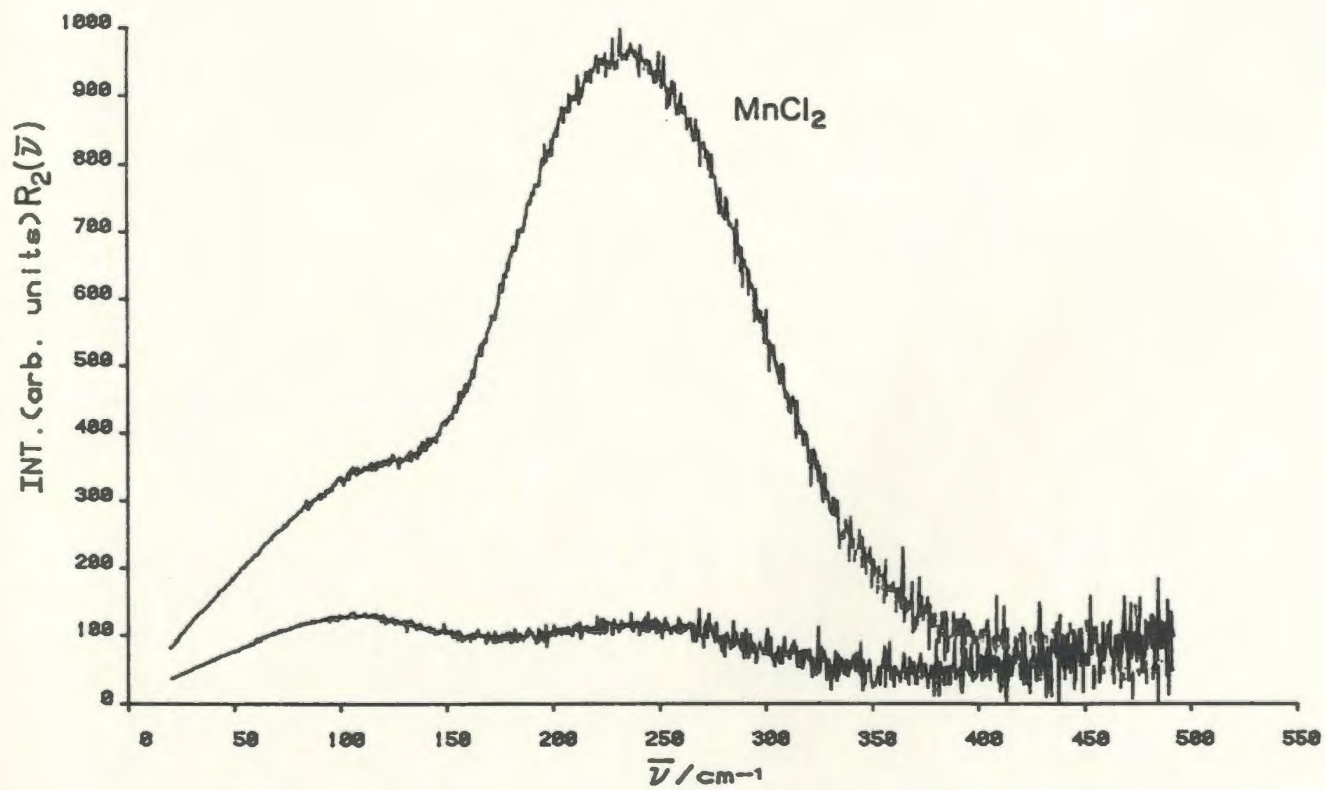
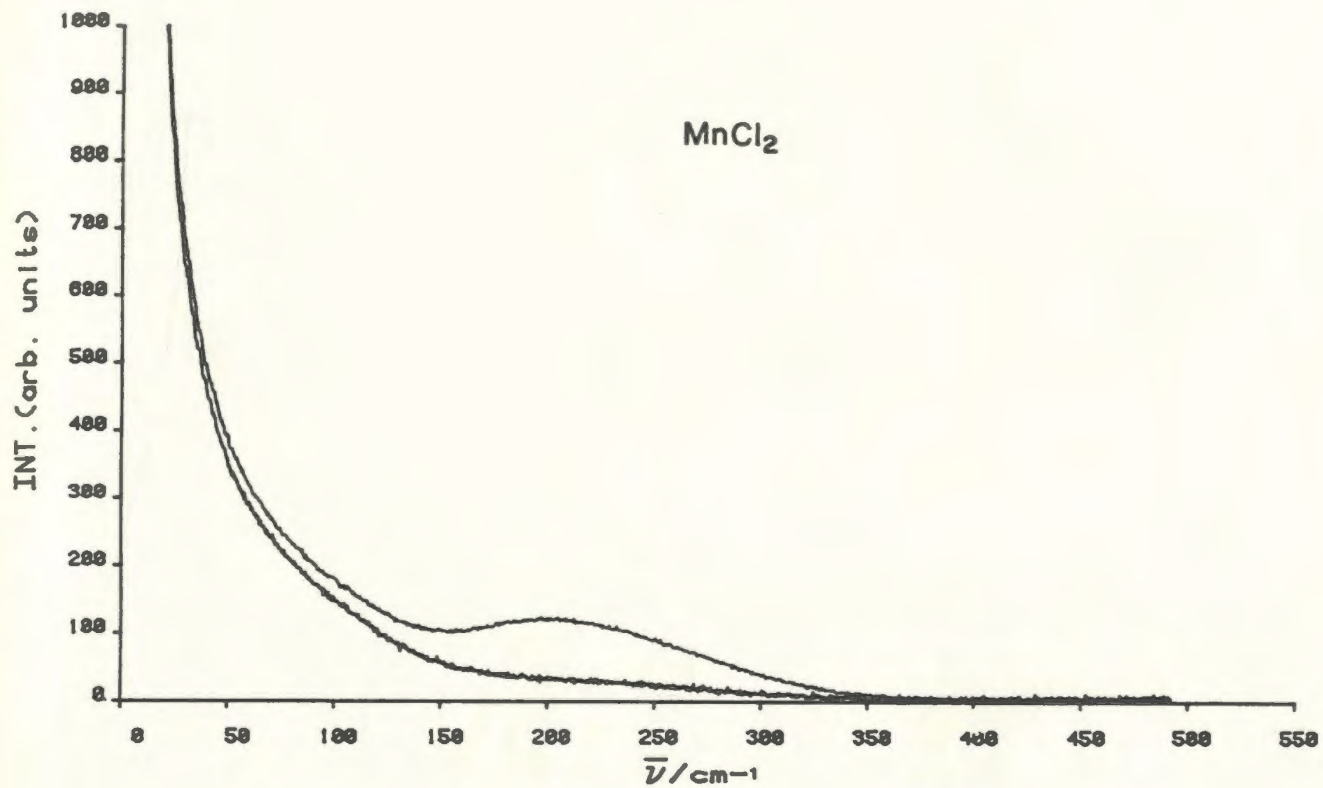




Figure 12. Raman spectra of molten  $\text{Cs}_2\text{MnCl}_4$  at 844 K,  $I_{||}$   
and  $I_{\perp}$ .

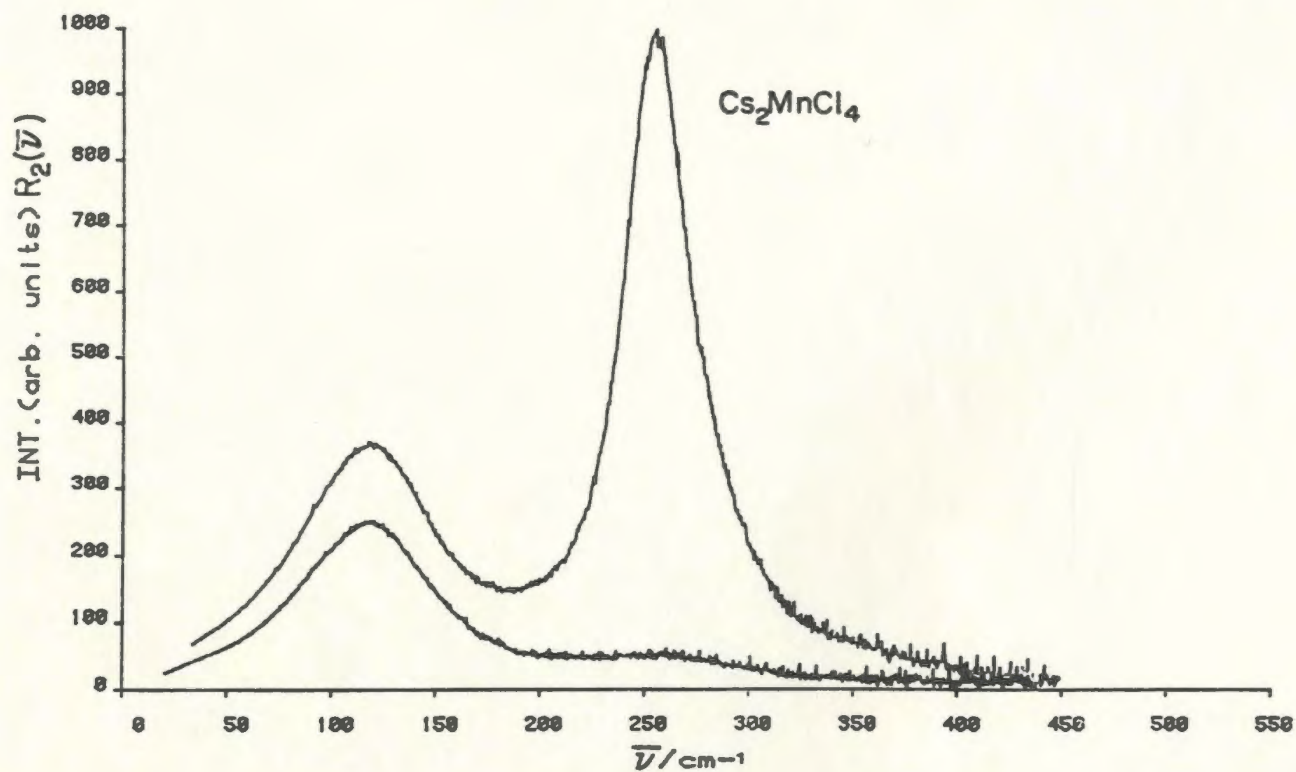
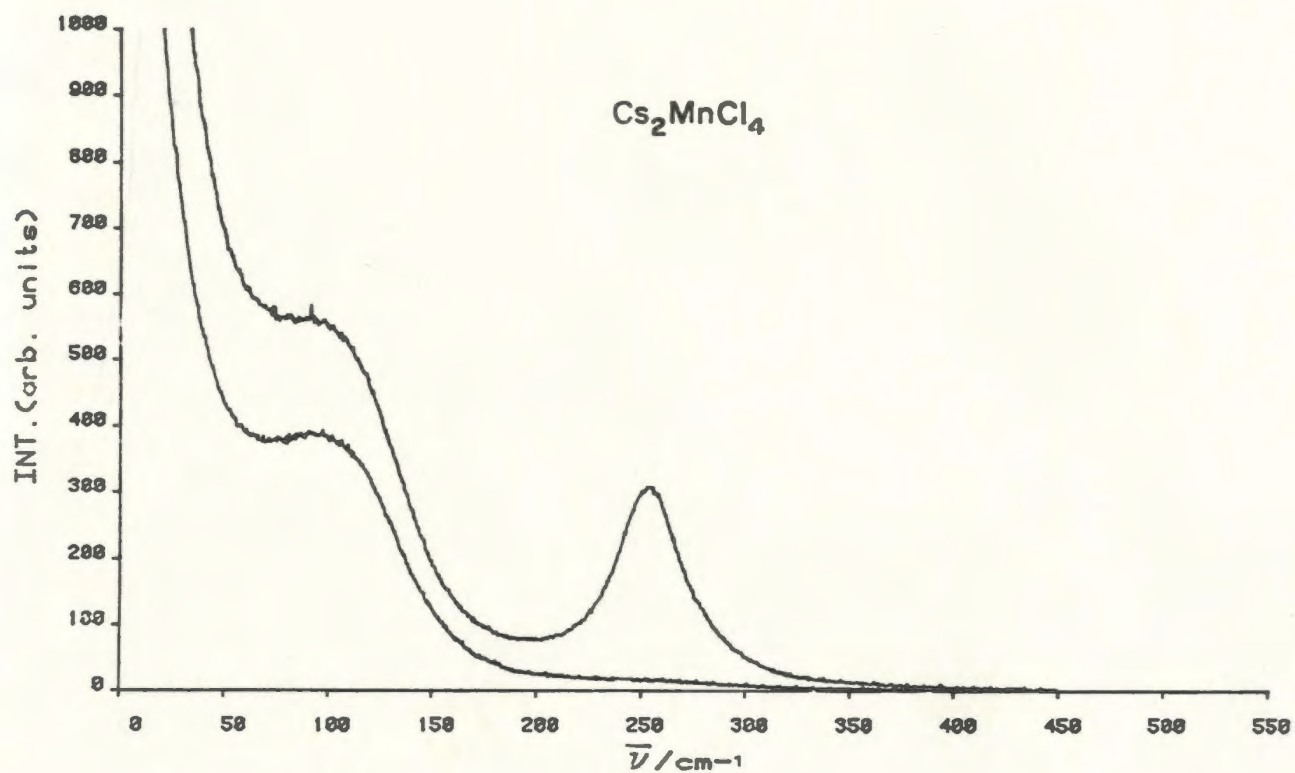


Figure 13. Raman spectra of molten  $\text{Cs}_3\text{MnCl}_5$  at 844 K,  $I_{||}$   
and  $I_{\perp}$ .



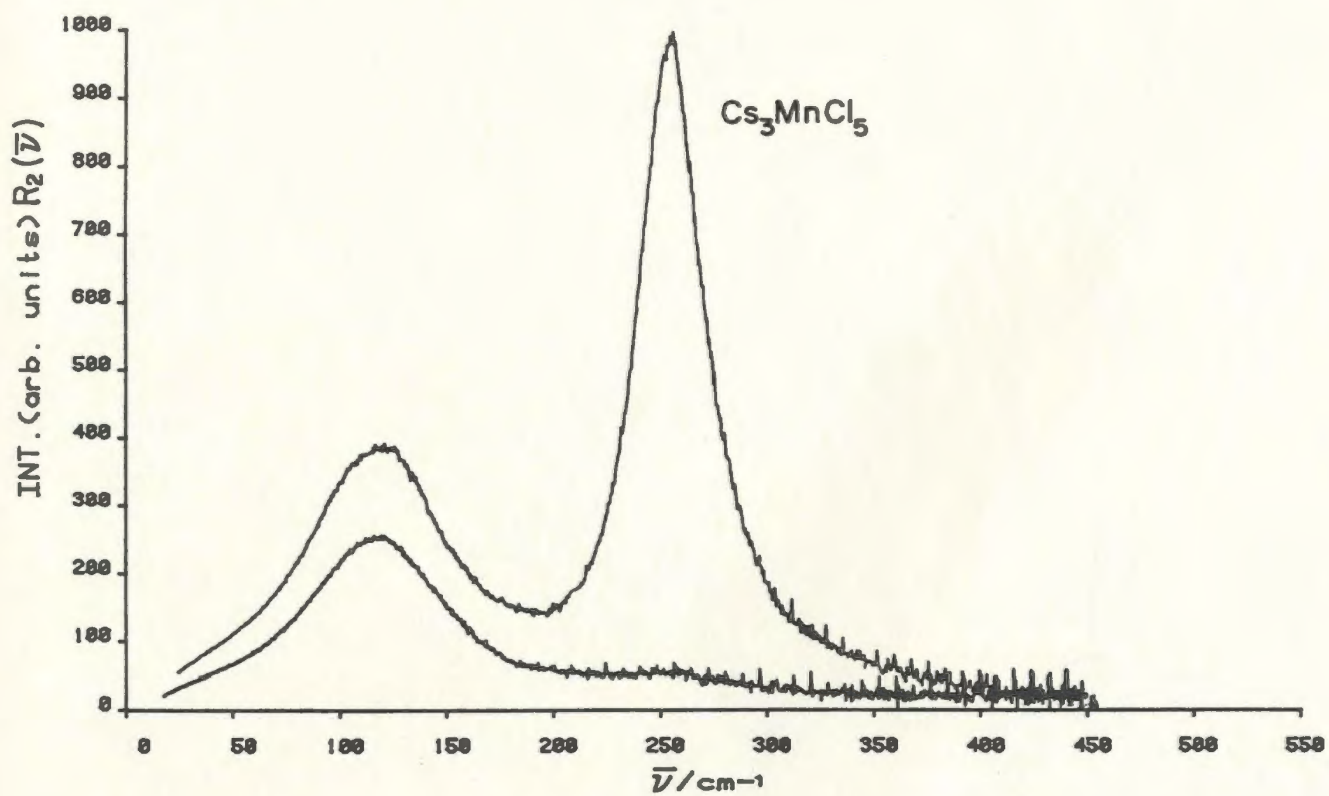
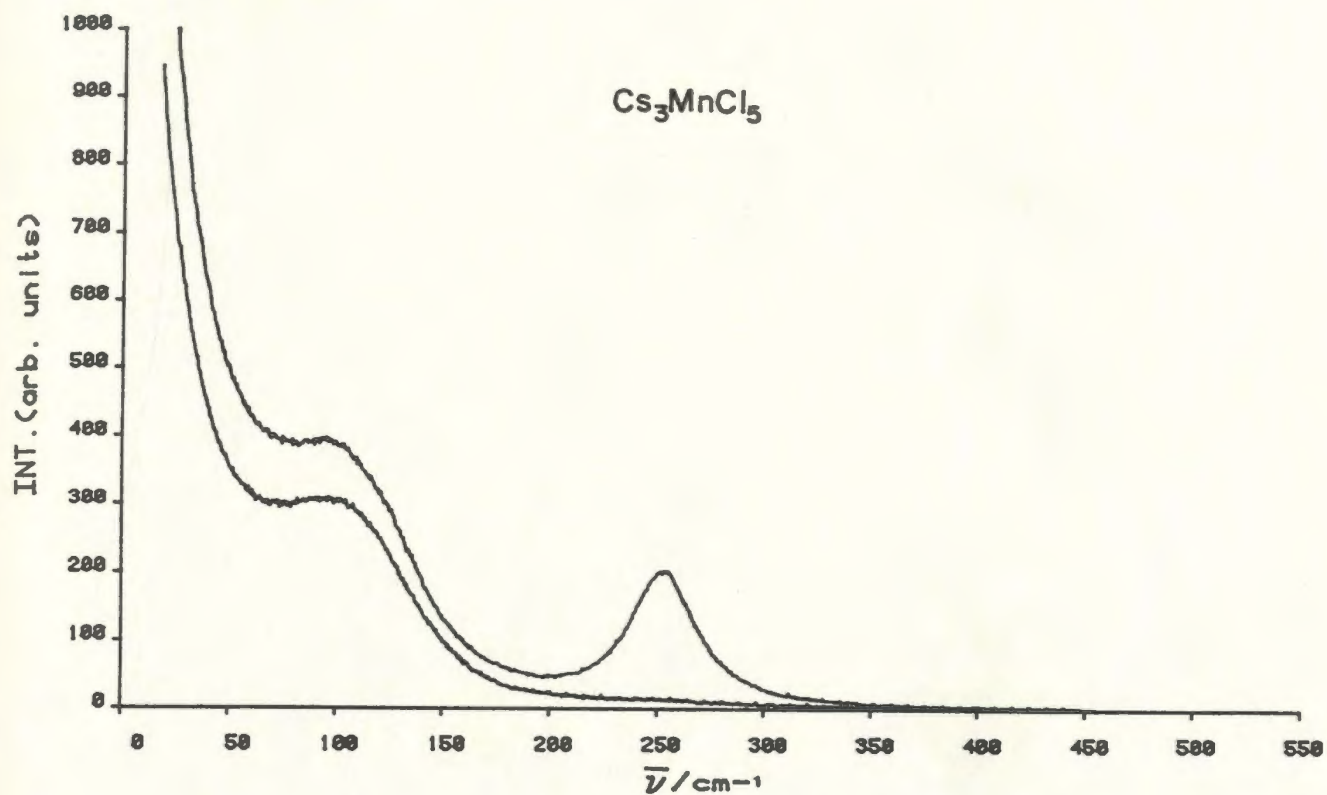


Figure 14. Raman spectra of molten  $\text{CsMnCl}_3$  at 916 K,  $I_{||}$   
and  $I_{\perp}$ .

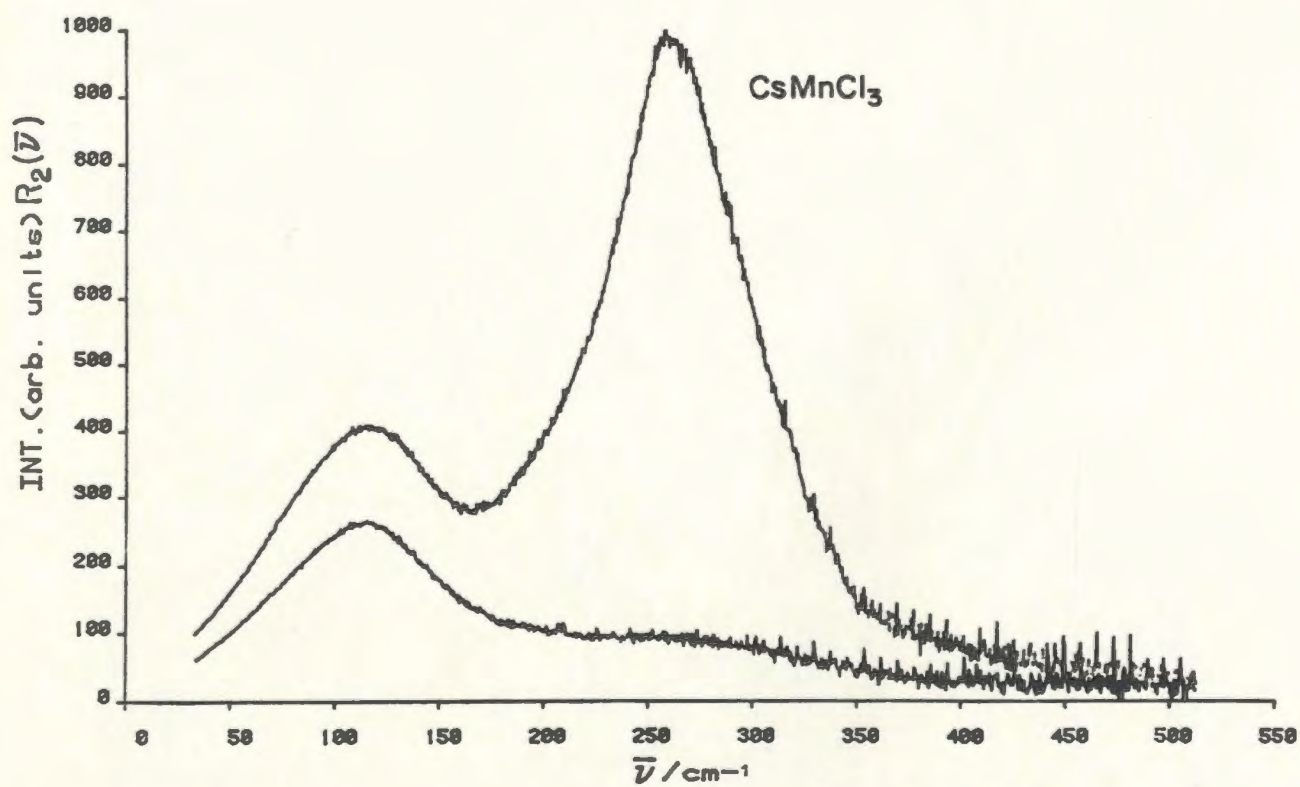
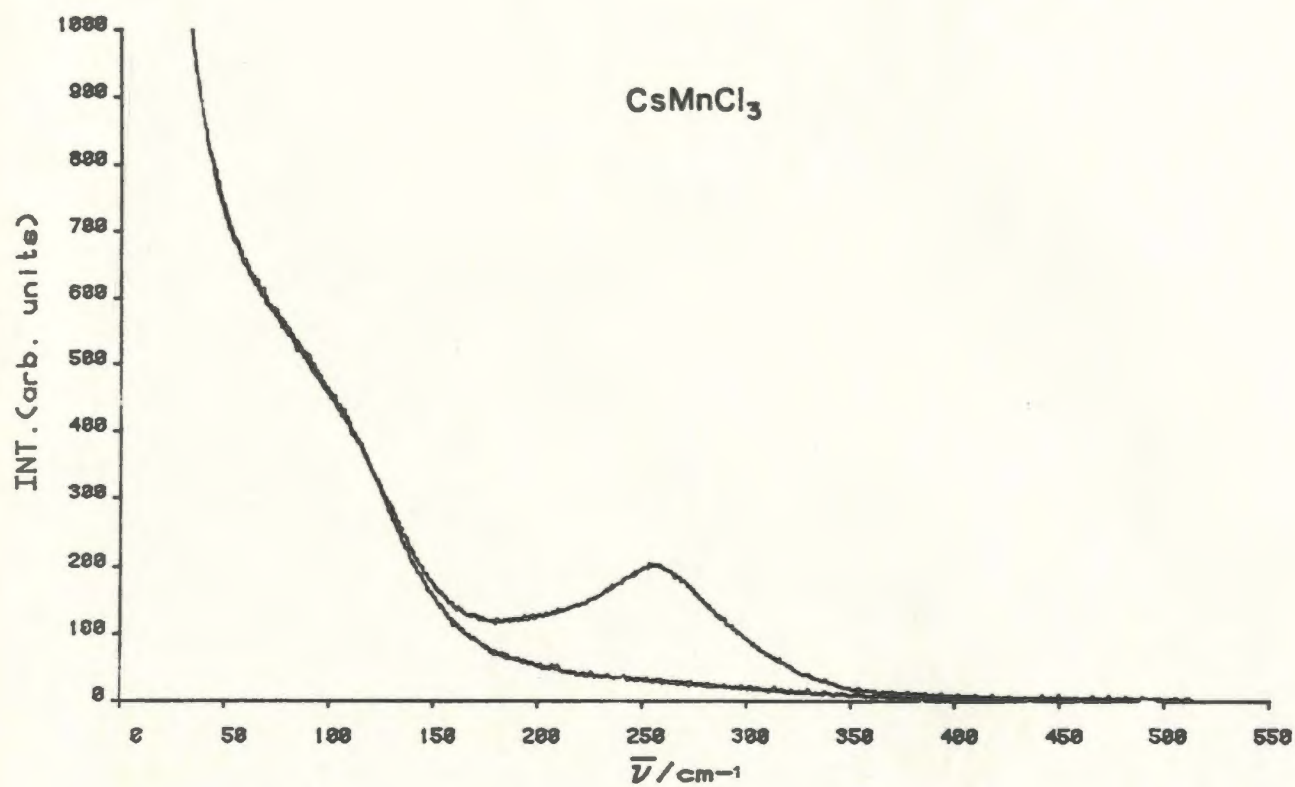




Figure 15. Raman spectra of molten  $\text{CsMn}_4\text{Cl}_9$  at 865 K,  $I_{||}$   
and  $I_{\perp}$ .

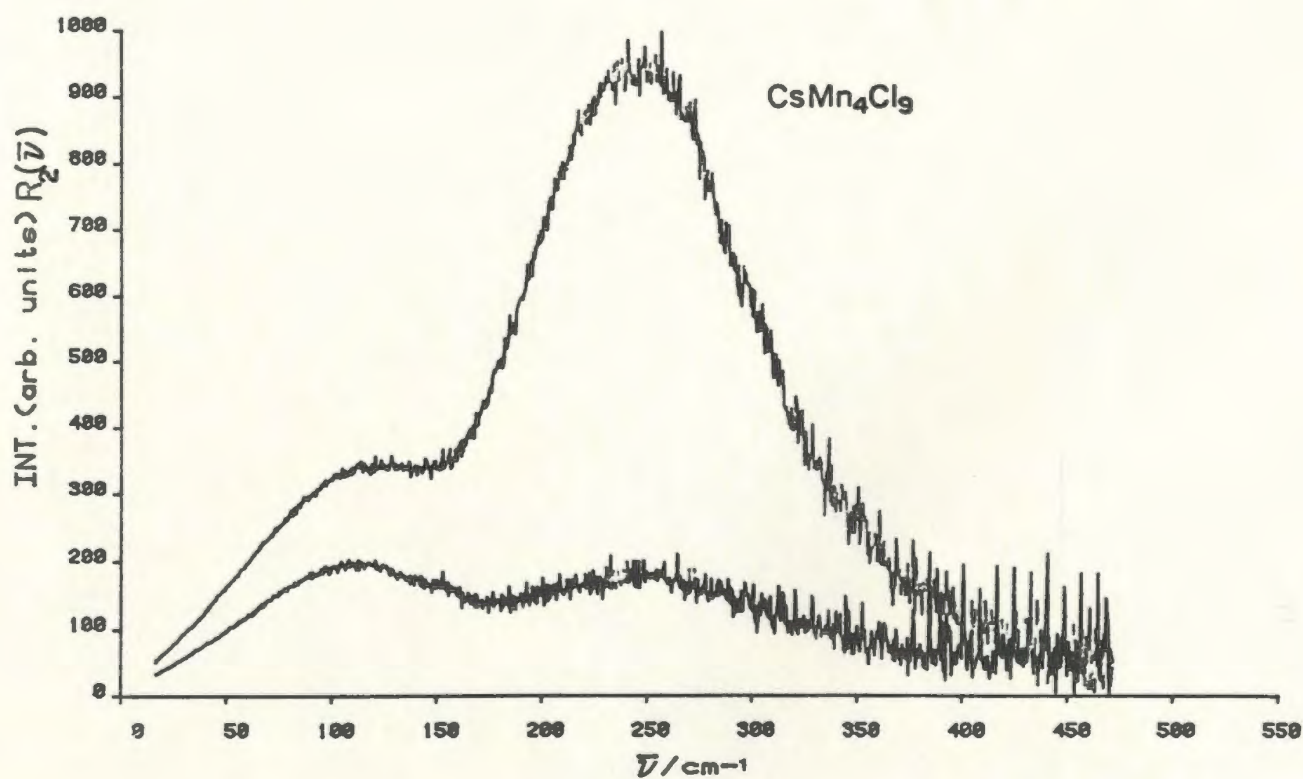
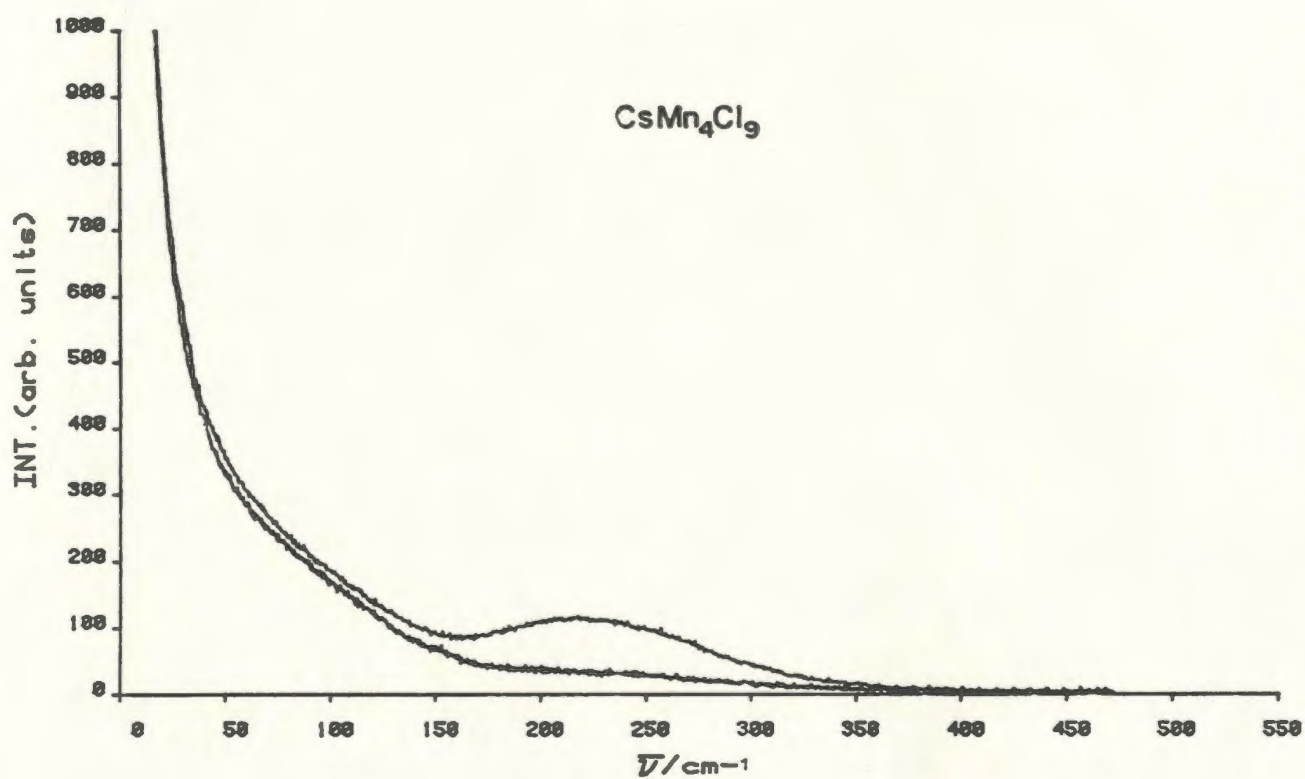


Figure 16. Effect of temperature on  $\nu_1$  mode of  $\text{Cs}_2\text{MnCl}_4$ .

A. Plot of band position ( $\text{cm}^{-1}$ ) vs temperature.

B. Plot of half band width ( $\text{cm}^{-1}$ ) vs temperature.



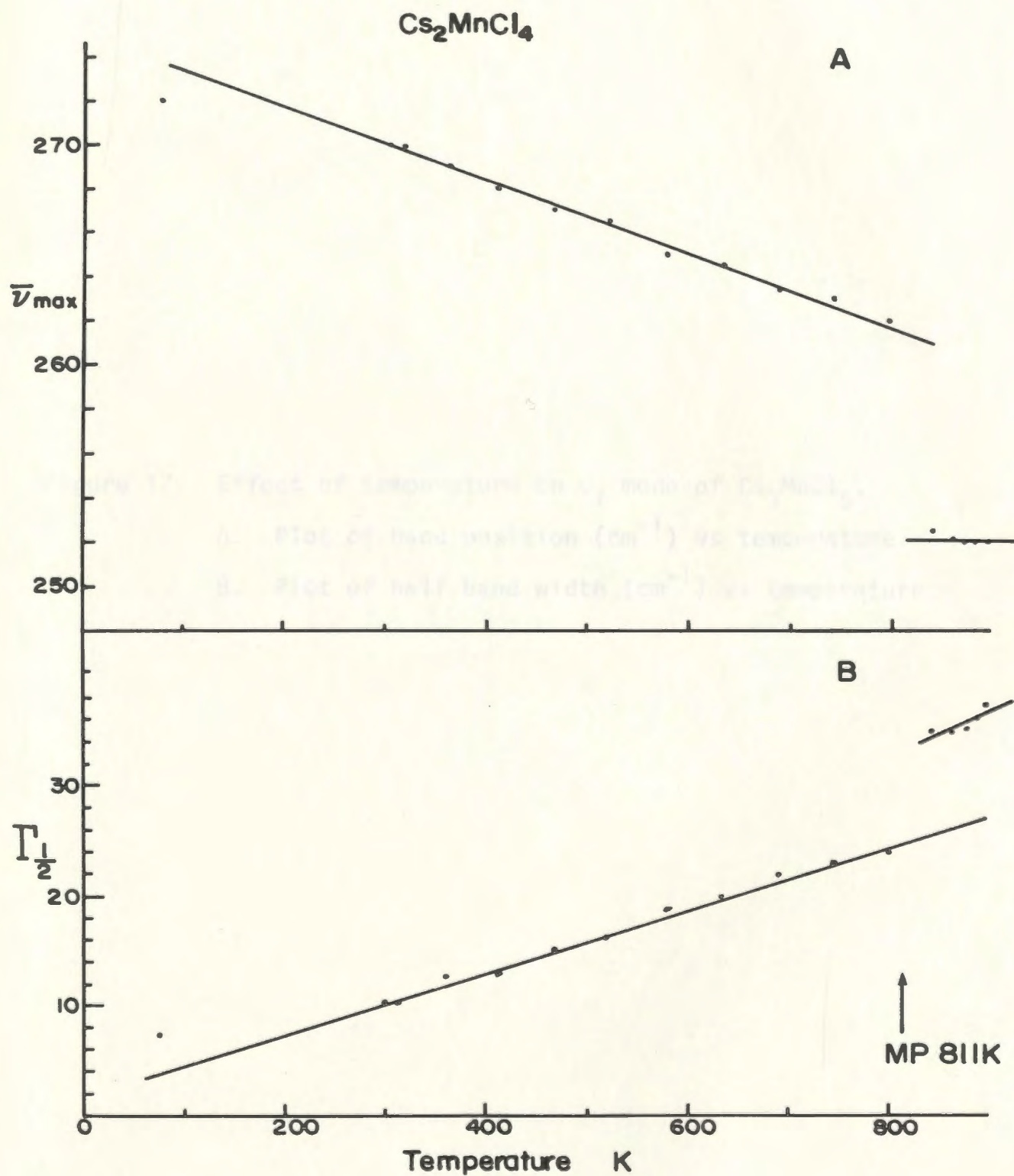


Figure 17. Effect of temperature on  $\nu_1$  mode of  $\text{Cs}_3\text{MnCl}_5$ .

A. Plot of band position ( $\text{cm}^{-1}$ ) vs temperature.

B. Plot of half band width ( $\text{cm}^{-1}$ ) vs temperature.

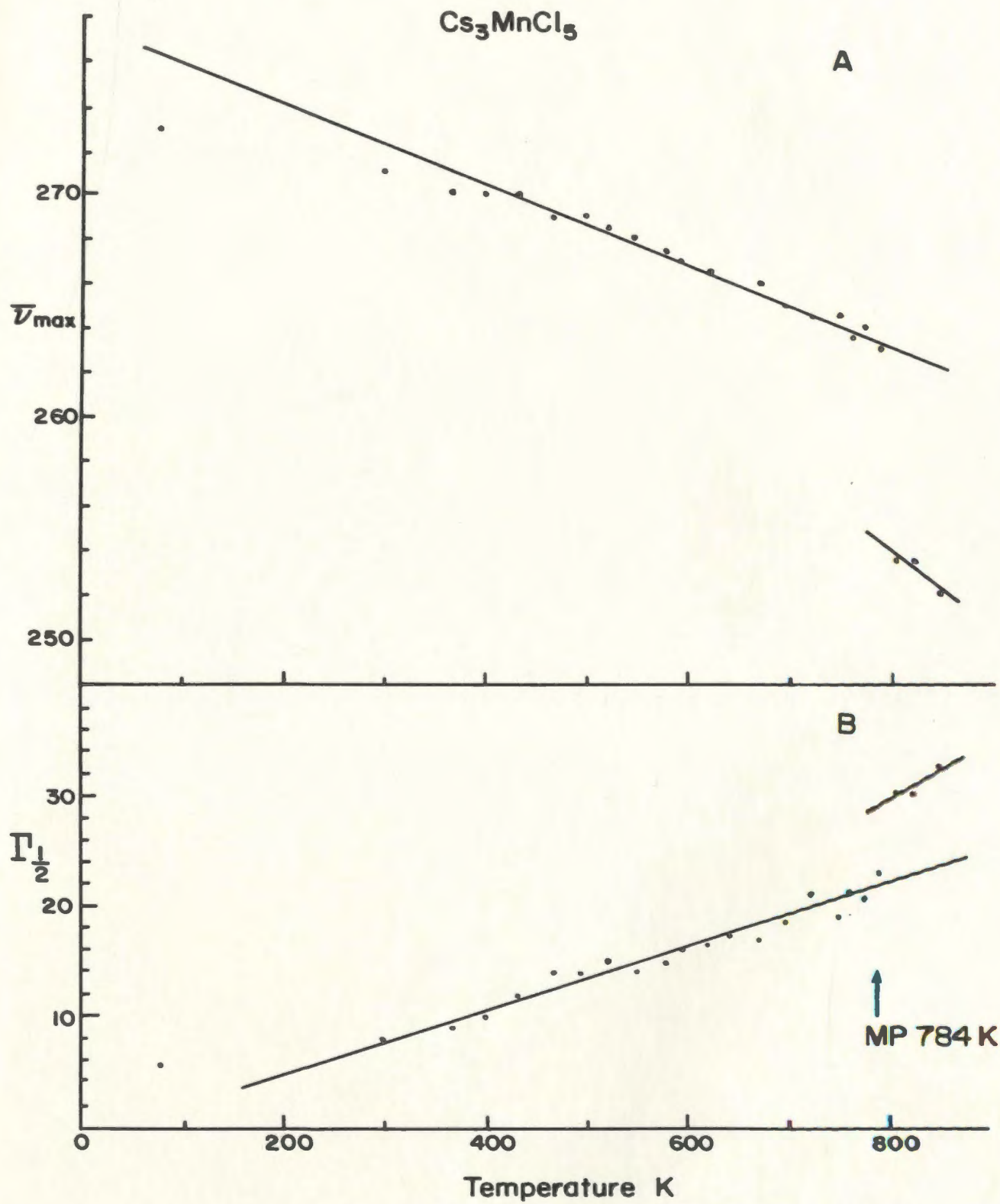




Figure 18. Isotropic Raman spectra of molten  $\text{MnCl}_2$ . The smooth line is the best-fit curve calculated with a single Gaussian\*Lorentzian function.

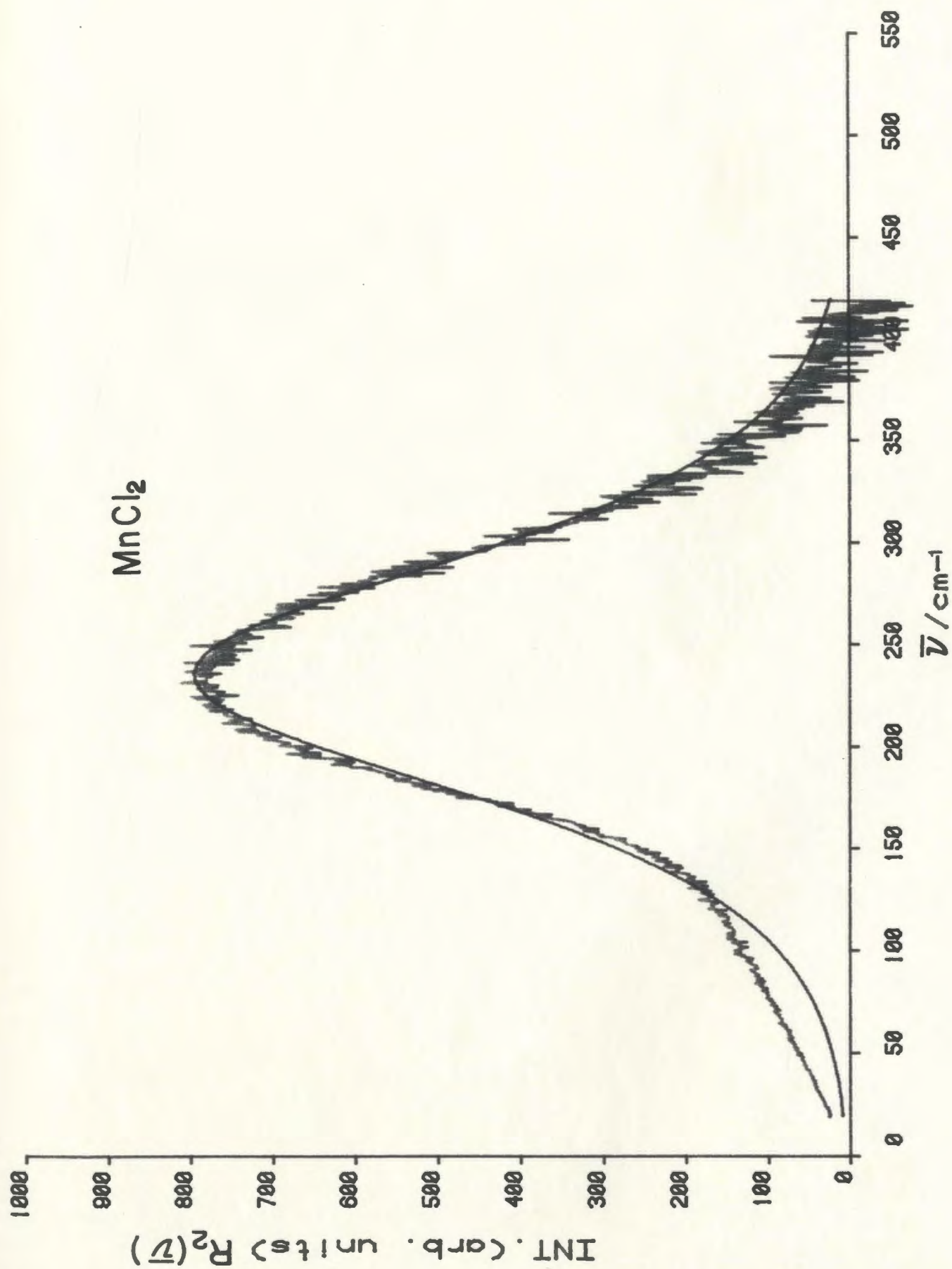


Figure 19. Isotropic Raman spectra of molten  $\text{Cs}_2\text{MnCl}_4$ . The smooth line is the best-fit curve calculated with a single Lorentzian function.



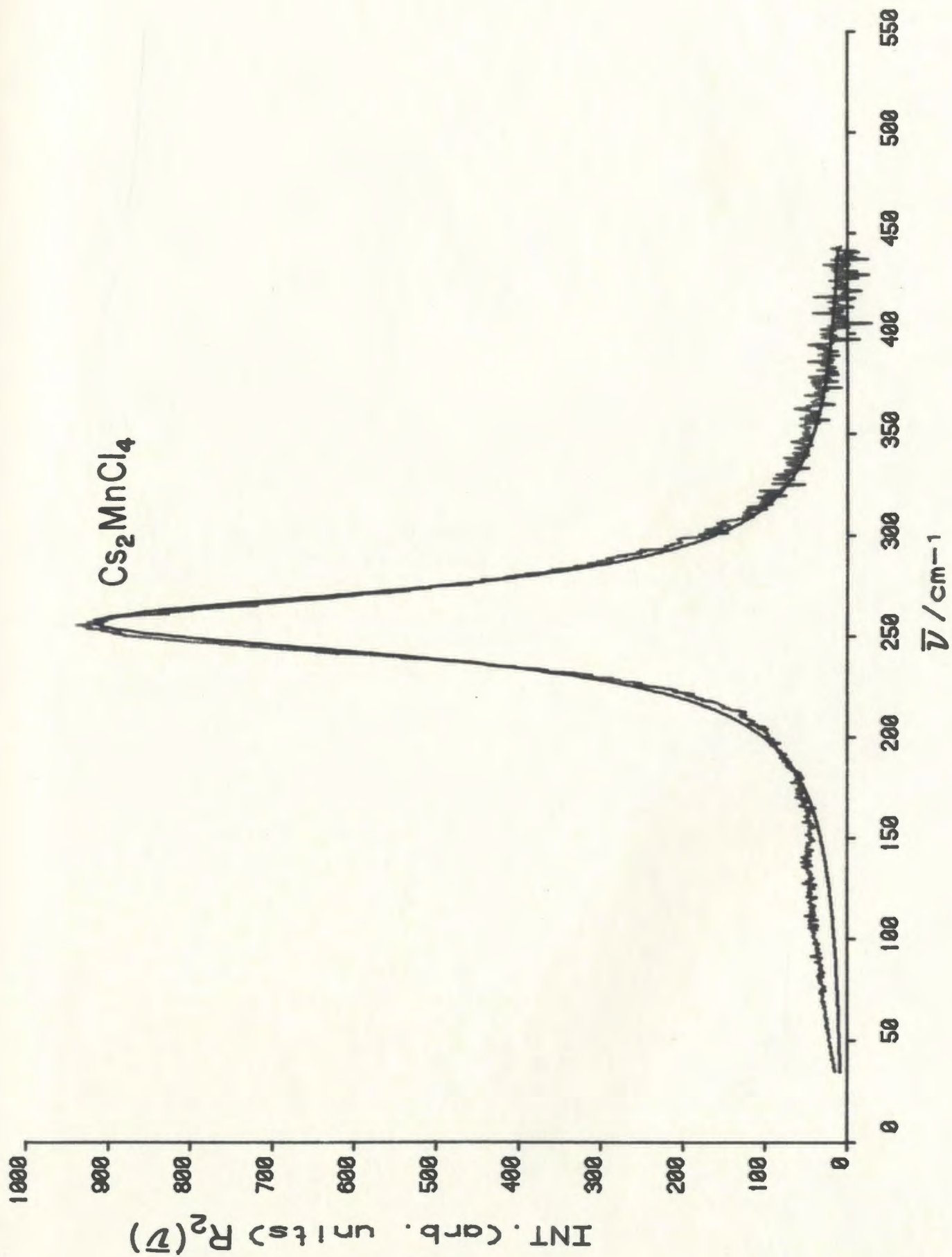


Figure 20. Isotropic Raman spectra of molten  $\text{Cs}_3\text{MnCl}_5$ . The smooth line is the best-fit curve calculated with a single Lorentzian function.

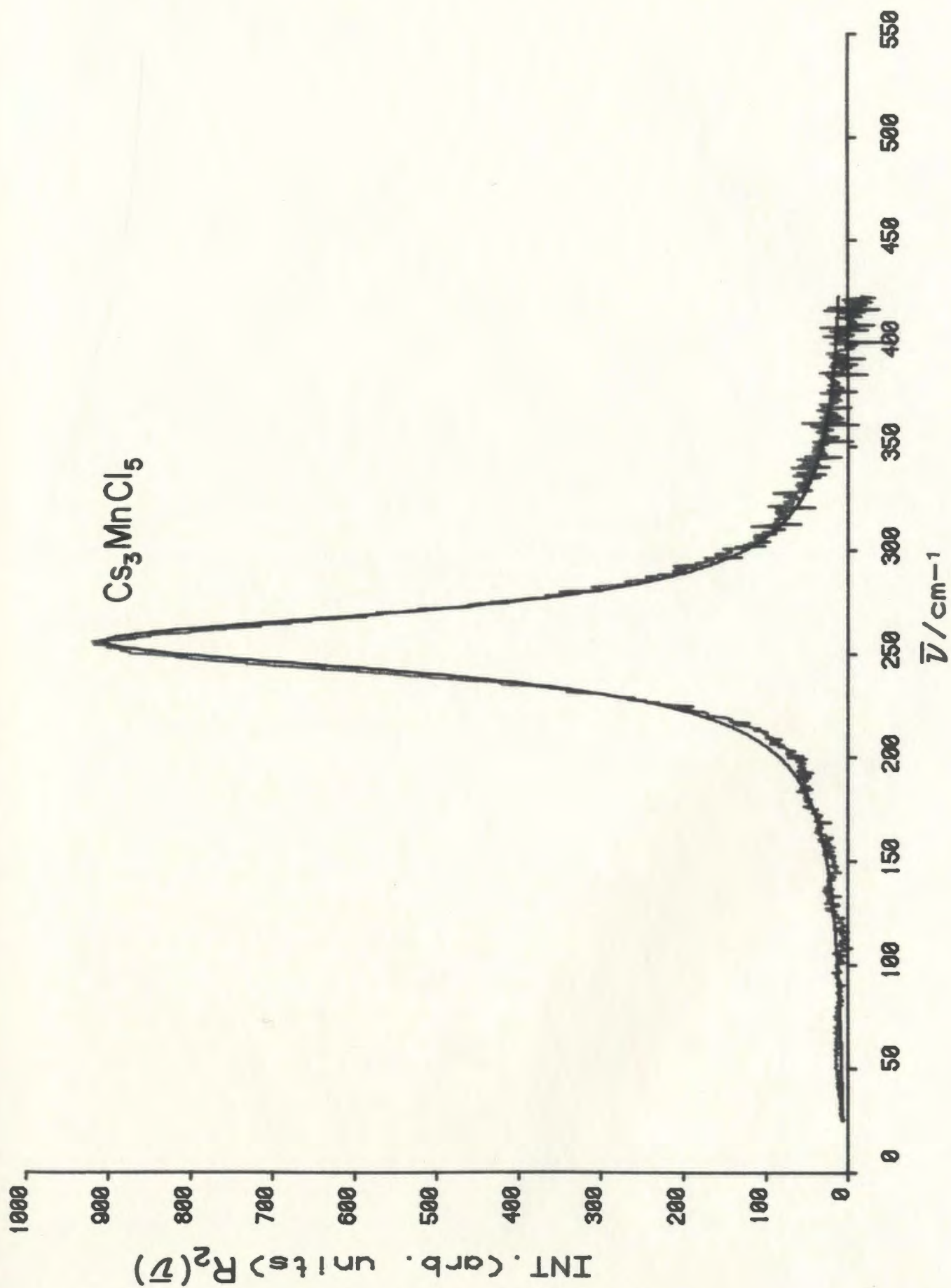




Figure 21. Isotropic Raman spectra of molten  $\text{CsMnCl}_3$ . The smooth line is the best-fit curve calculated with a single Gaussian\*Lorentzian function.

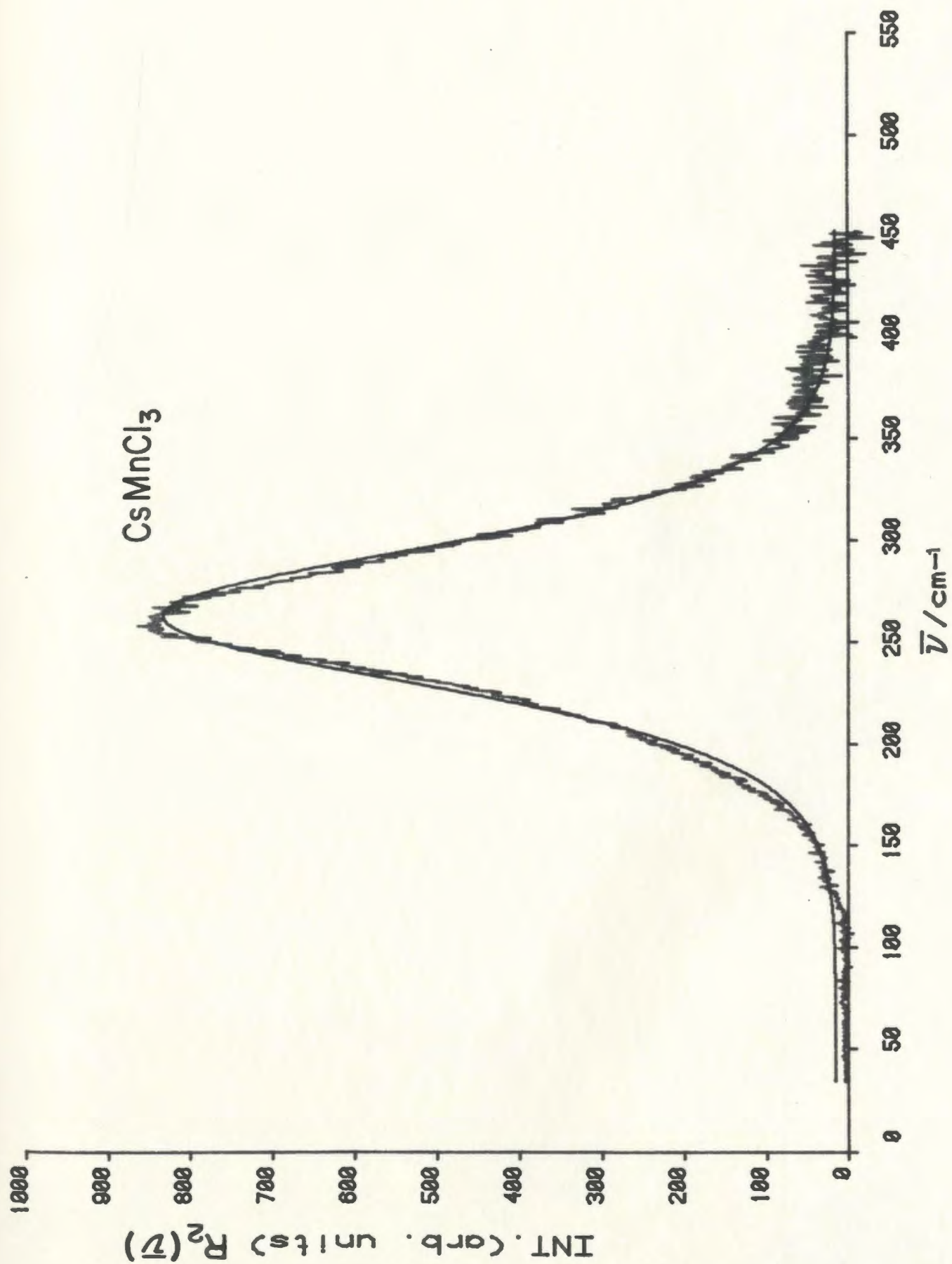


Figure 22. Isotropic Raman spectra of molten  $\text{CsMnCl}_3$ . The smooth line is the best-fit curve calculated with a single Lorentzian function.



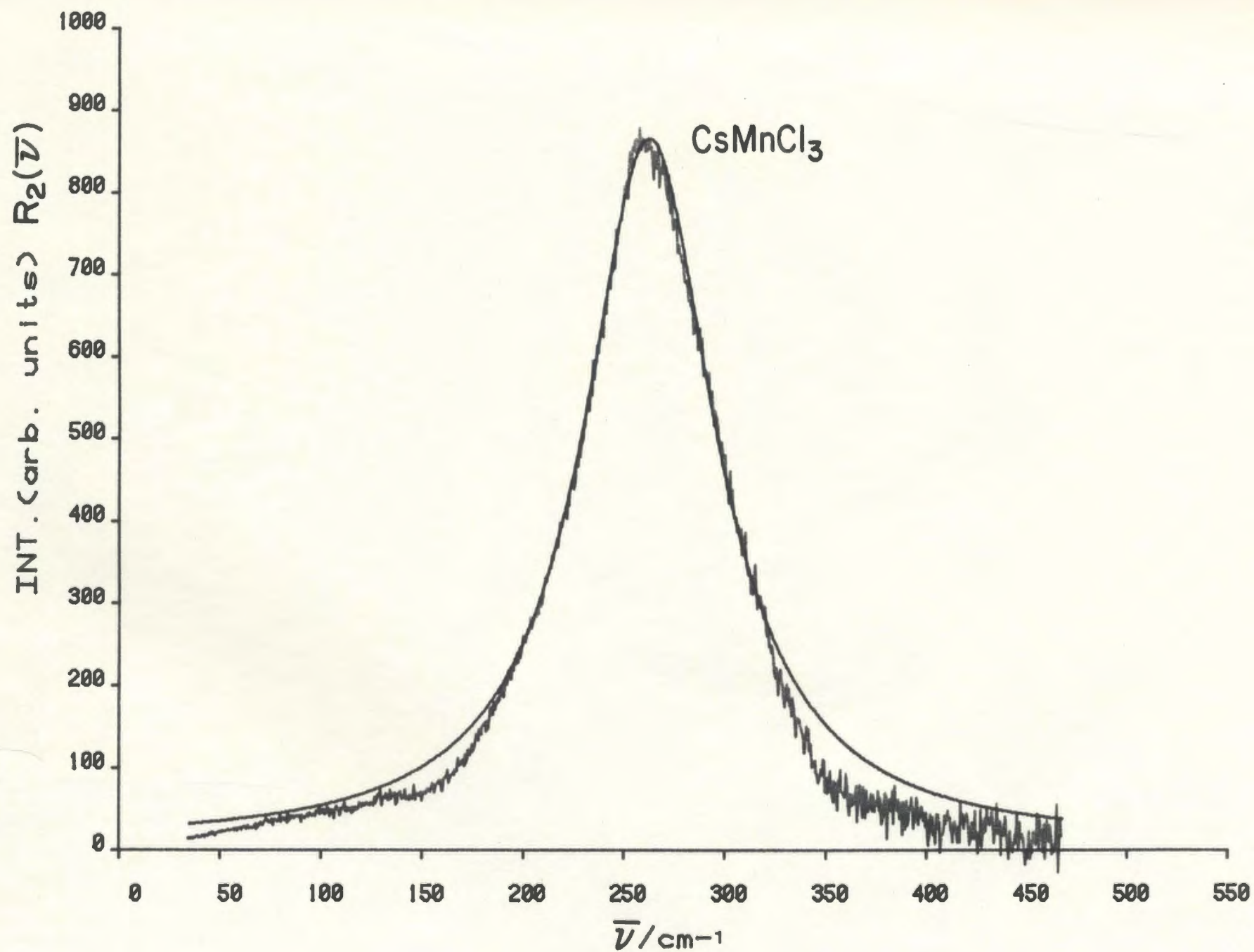
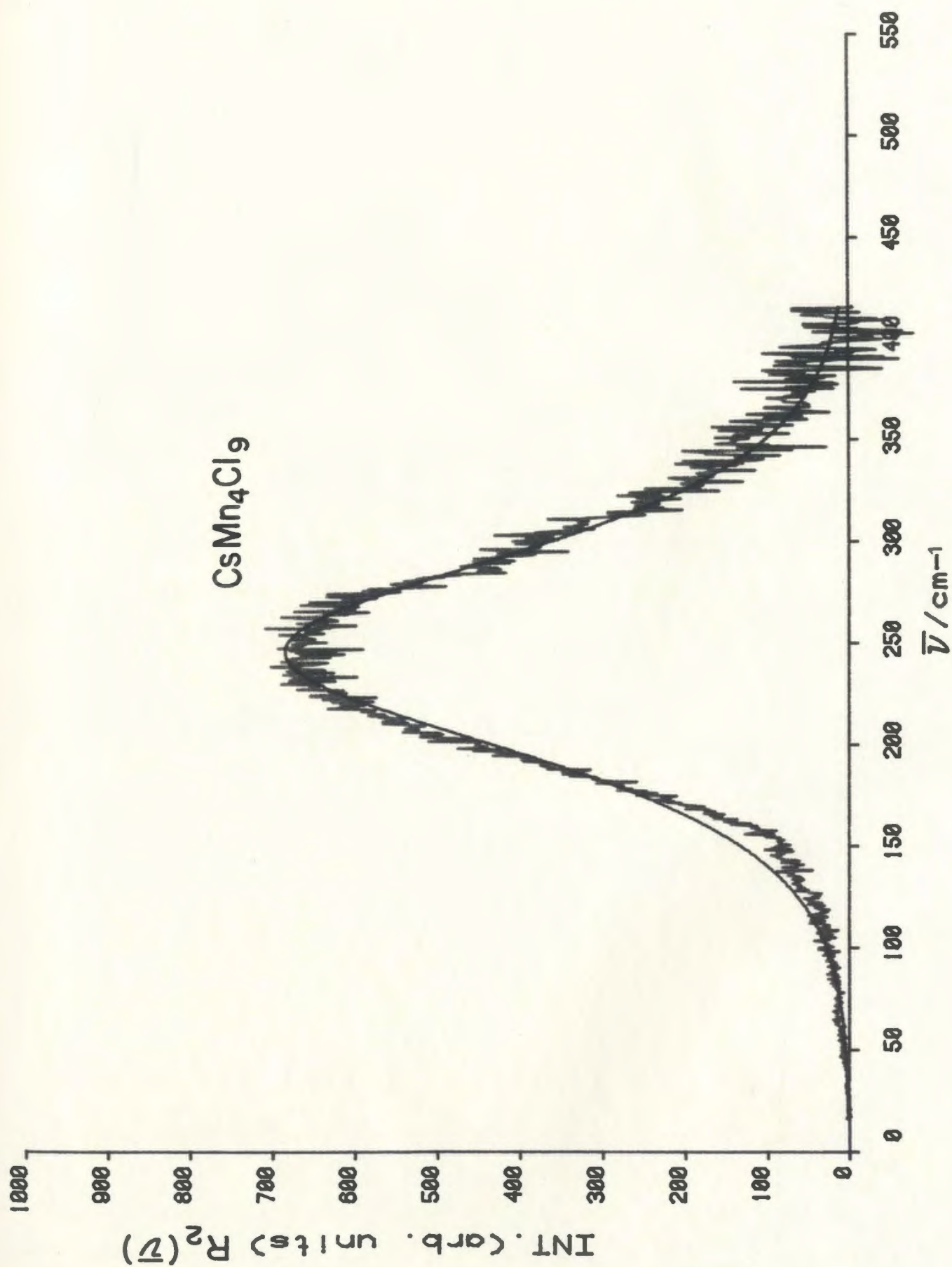


Figure 23. Isotropic Raman spectra of molten  $\text{CsMn}_4\text{Cl}_9$ . The smooth line is the best-fit curve calculated with a single Gaussian\*Lorentzian function.





The polarized peak from the  $R_2(\bar{\nu})$  spectrum was fitted to Lorentzian and Gaussian\*Lorentzian functions. The results are shown in figures 18, 19, 20, 21, 22, and 23. The frequency ( $\text{cm}^{-1}$ ), intensity, half band width ( $\text{cm}^{-1}$ ) and type of fit are shown in Table 20. For  $\text{CsMnCl}_3$  both the Lorentzian and Gaussian\*Lorentzian fits are given to show that the results are not very dependent on the choice of function.

#### 4.2.2 $\text{MnCl}_2$ -RbCl Melts

The Raman spectra of  $\text{RbMnCl}_3$ ,  $\text{Rb}_2\text{MnCl}_4$ ,  $\text{RbCl:MnCl}_2$  (3:1), and  $\text{Rb}_3\text{Mn}_2\text{Cl}_7$  melts are shown in figures 24, 25, 26, and 27. The results indicate the presence of  $\text{MnCl}_4^{2-}$  species. An isolated  $\text{MnCl}_4^{2-}$  tetrahedral ion is proposed for melts of composition  $\text{MnCl}_2 \cdot n\text{RbCl}$  ( $n \geq 2$ ) but for  $\text{RbMnCl}_3$  and  $\text{Rb}_3\text{Mn}_2\text{Cl}_7$  melts ( $n < 2$ ) a tetrahedral species with corner sharing are expected. The half band width of the stretching mode ( $\nu_1$ ) increased by increasing  $\text{MnCl}_2$  content. The  $\nu_3$  peak is too weak to be observed, while  $\nu_2$  and  $\nu_4$  are observed as overlapped peaks in the region  $70\text{-}135 \text{ cm}^{-1}$ .

The polarized peak from the  $R_2(\bar{\nu})$  spectrum was fitted to Gaussian\*Lorentzian and Lorentzian functions. The results are shown in figures 28, 29, 30, and 31 and tabulated in Table 21.

#### 4.2.3 $\text{MnCl}_2$ -KCl Melts

The Raman spectra of  $\text{KMnCl}_3$ ,  $\text{KCl:MnCl}_2$  (2:1),  $\text{KCl:MnCl}_2$  (3:1),  $\text{K}_3\text{Mn}_2\text{Cl}_7$ , and  $\text{K}_4\text{MnCl}_6$  melts are shown in figures 32, 33, 34, 35, and 36. One polarized peak ( $\nu_1$ ) appears in each spectrum in the range  $200\text{-}325 \text{ cm}^{-1}$ ,  $\nu_2$  and  $\nu_4$  are observed in the region  $70\text{-}140 \text{ cm}^{-1}$ ,  $\nu_3$  appear around  $\sim 300 \text{ cm}^{-1}$  but is weak to be observed. The data indicate

Table 21. Summary of results of curve resolution analysis for  
MnCl<sub>2</sub>-RbCl Melts.

Compound	Frequency (cm <sup>-1</sup> )	Intensity	Half band width (cm <sup>-1</sup> )	Function
RbCl:MnCl <sub>2</sub> (3:1)	254.4	890	41.0	L
Rb <sub>2</sub> MnCl <sub>4</sub>	258.0	918	42.5	L
Rb <sub>3</sub> Mn <sub>2</sub> Cl <sub>7</sub>	259.6	869	62.0	L
RbMnCl <sub>3</sub>	252.1	828	85.1	G * L

G: Gaussian, L: Lorentzian

Figure 24. Raman spectra of molten  $\text{RbMnCl}_3$  at 878 K,  $I_{||}$   
and  $I_{\perp}$ .



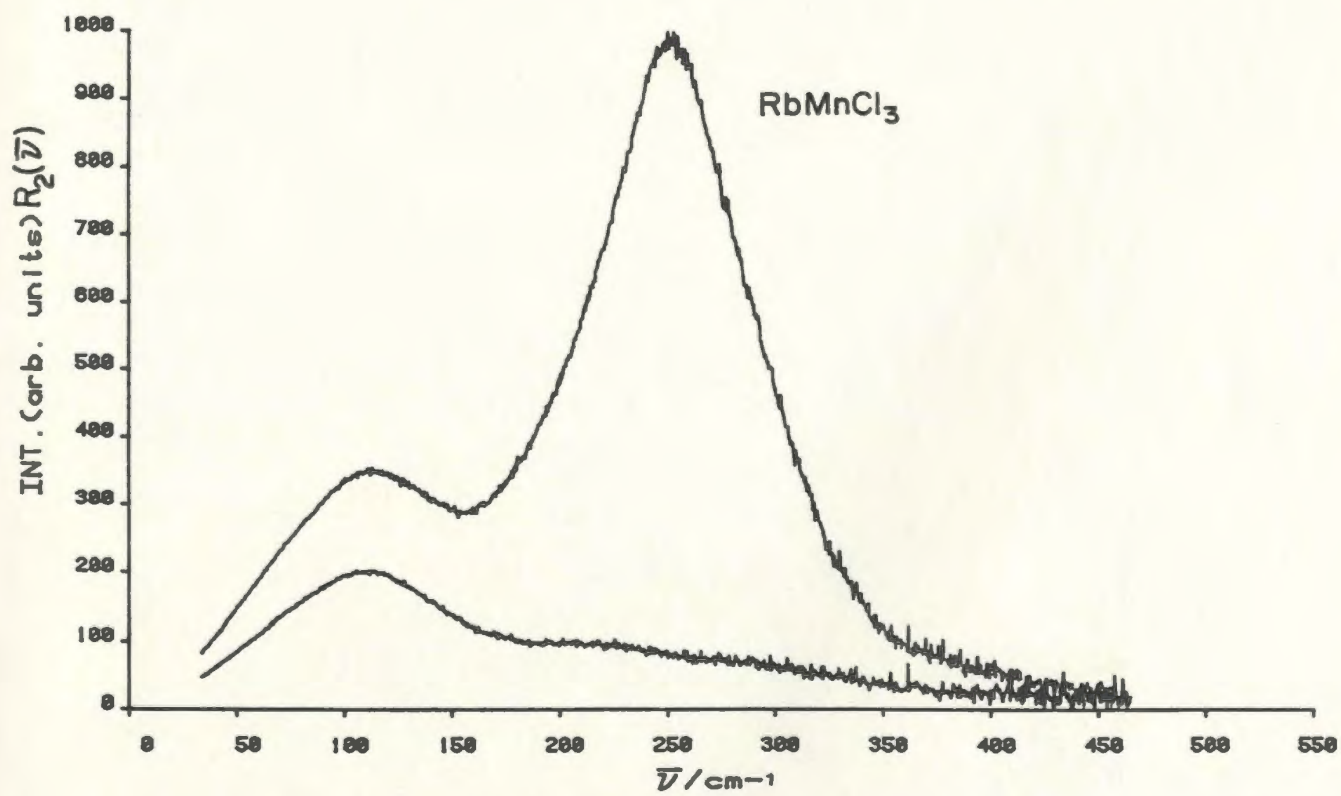
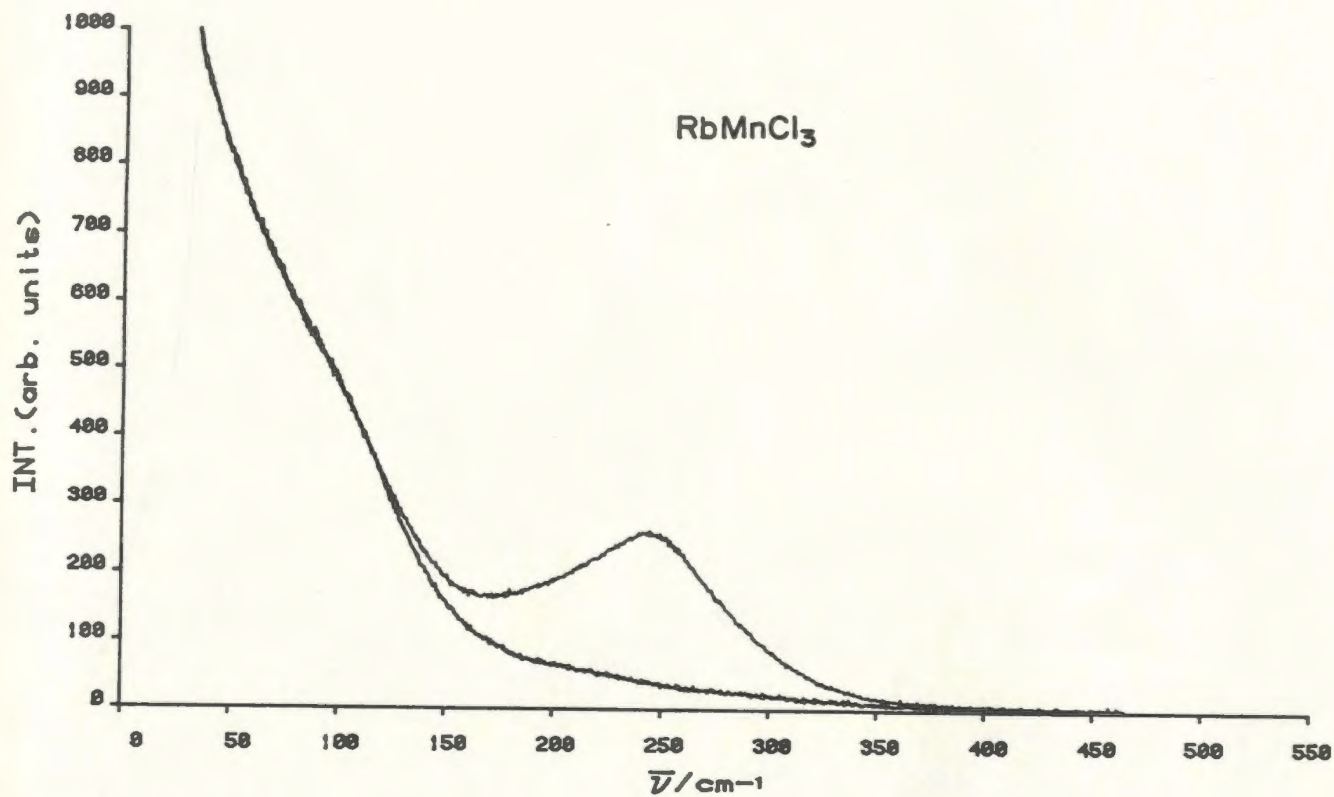


Figure 25. Raman spectra of molten  $\text{Rb}_2\text{MnCl}_4$  at 753 K,  $I_{||}$   
and  $I_{\perp}$ .

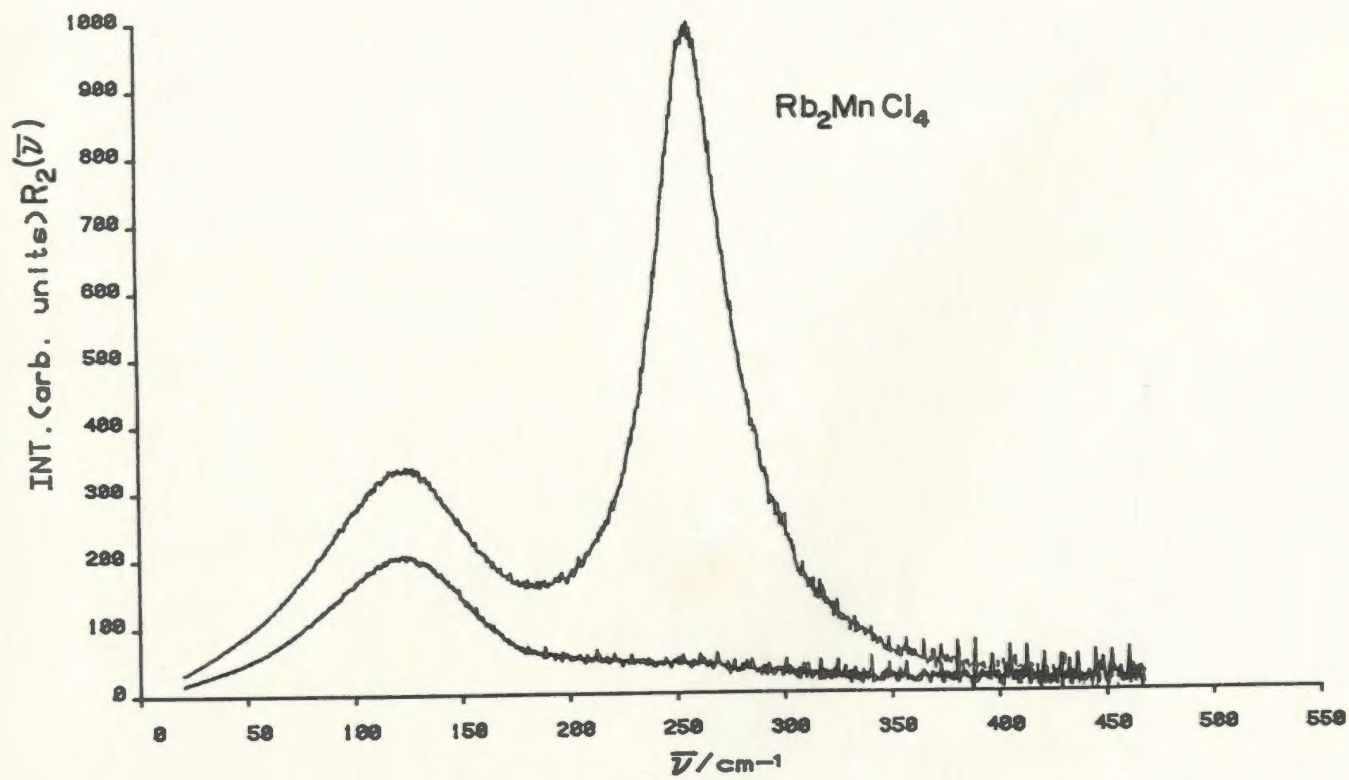
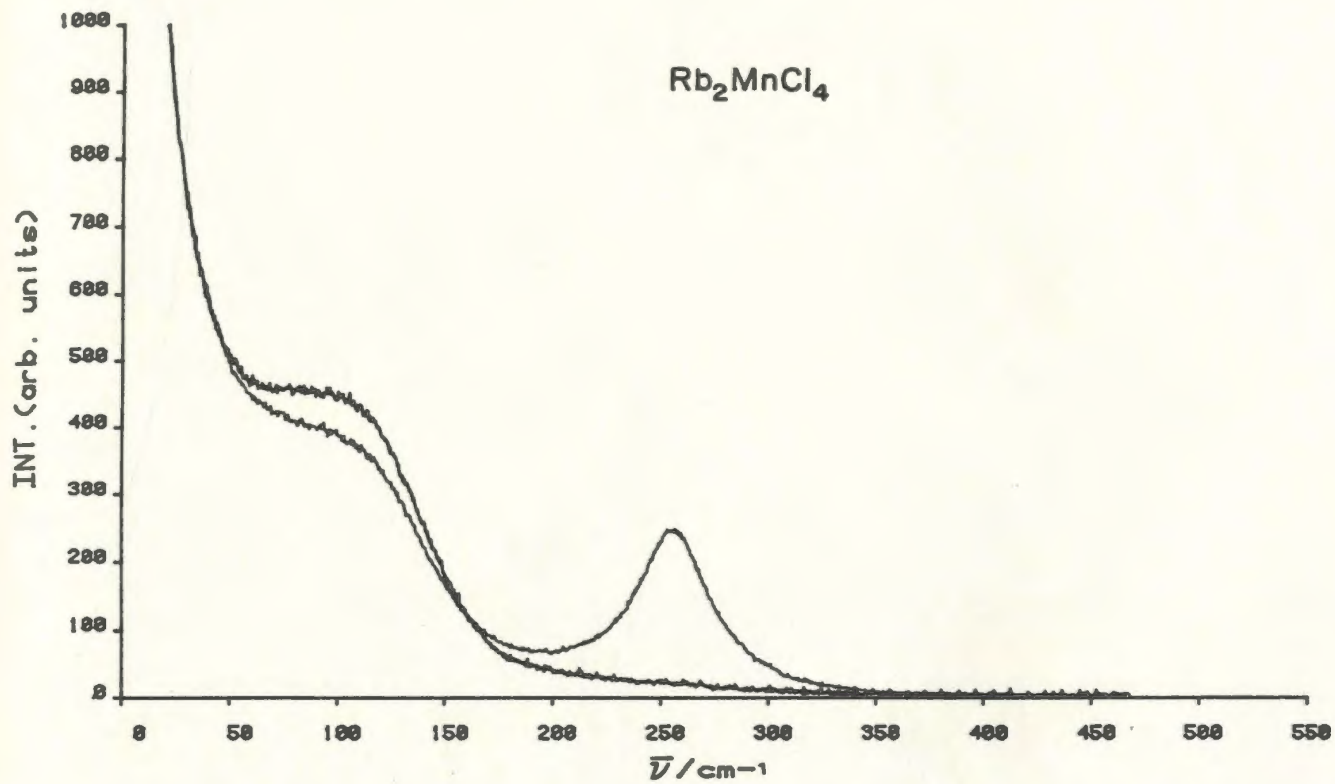




Figure 26. Raman spectra of molten  $\text{RbCl}:\text{MnCl}_2$  (3:1) at  
882 K,  $I_{||}$  and  $I_{\perp}$ .

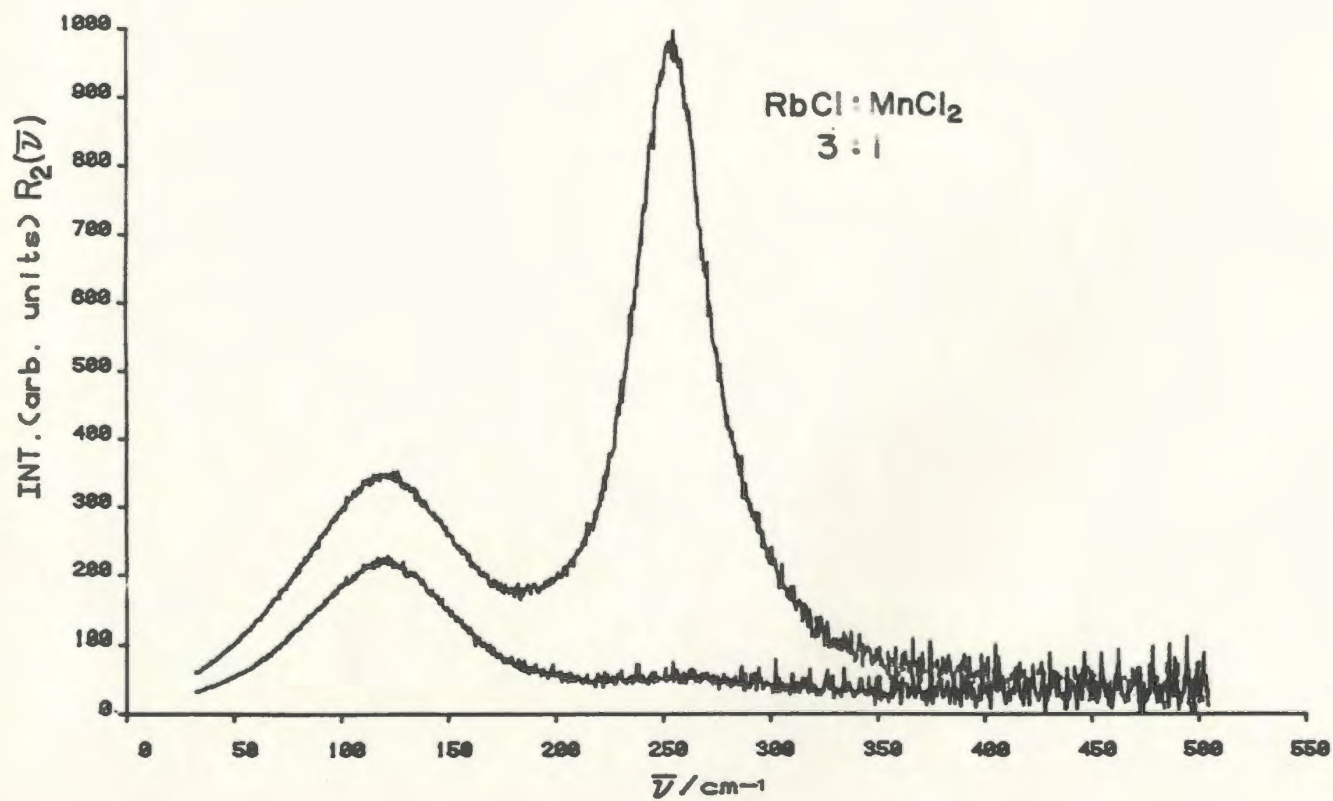
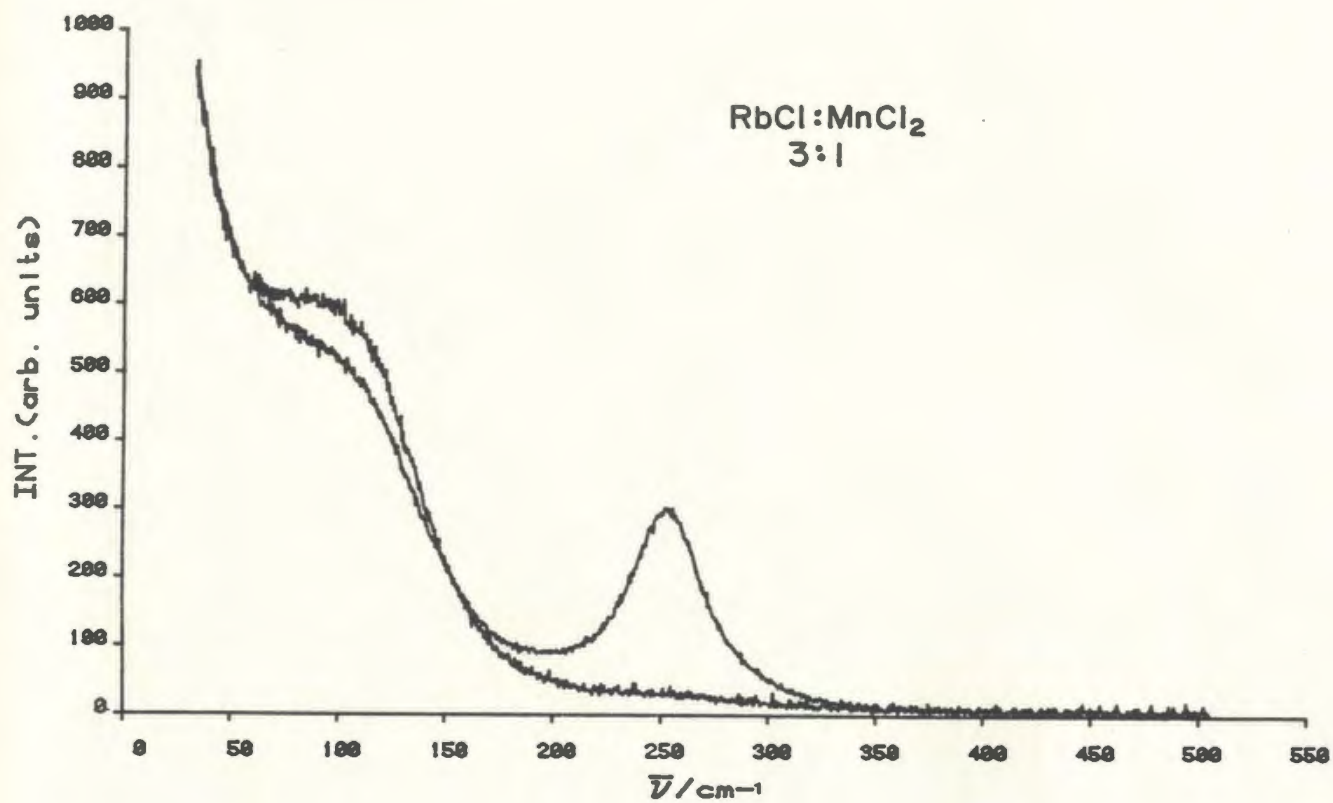


Figure 27. Raman spectra of molten  $\text{Rb}_3\text{Mn}_2\text{Cl}_7$  at 889 K,  
 $I_{||}$  and  $I_{\perp}$ .



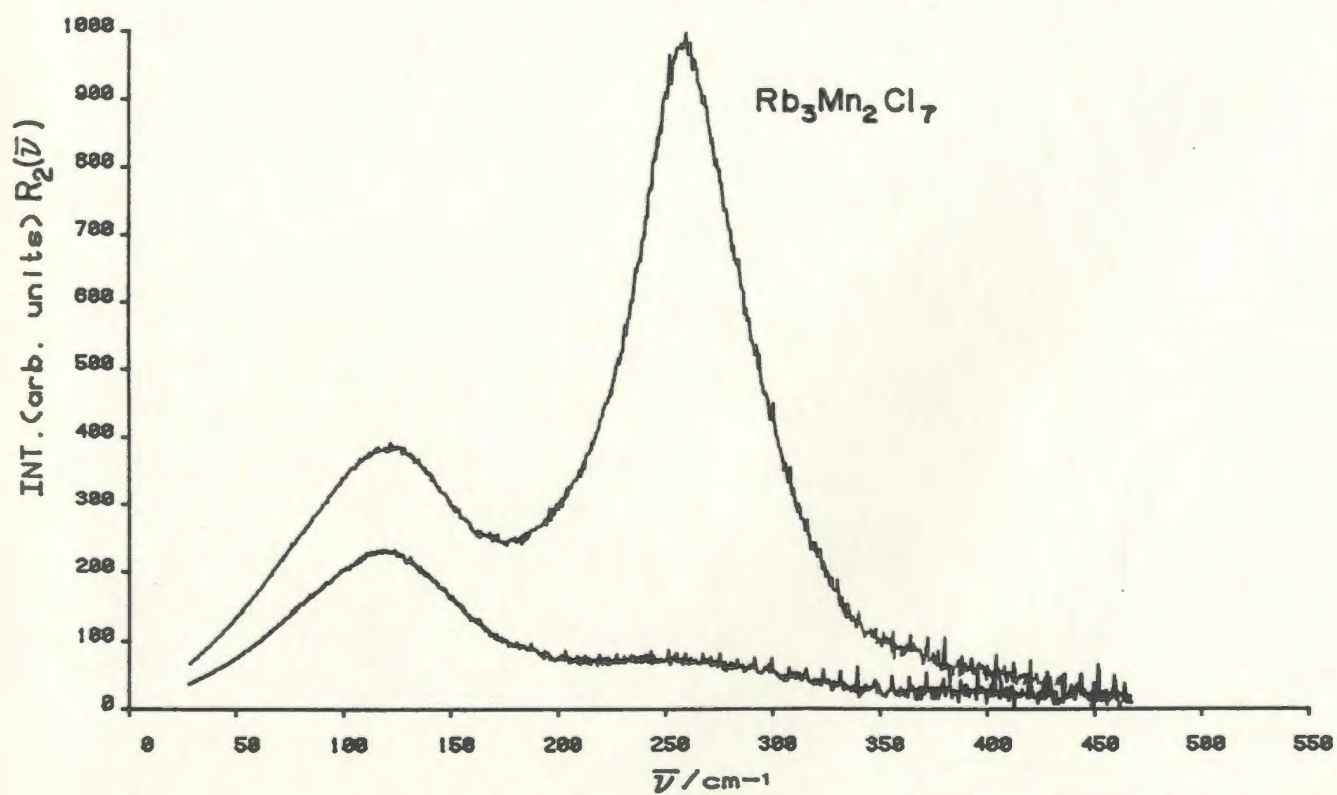
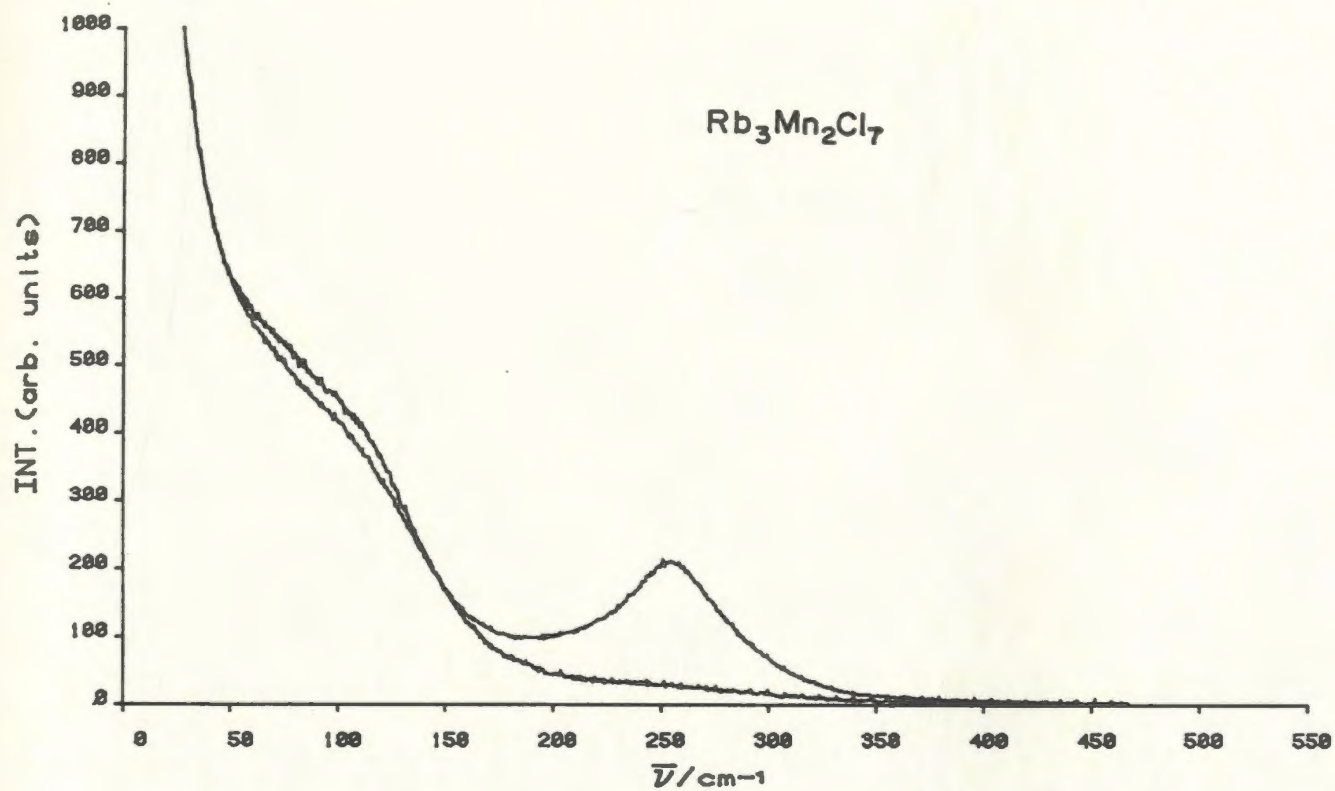


Figure 28. Isotropic Raman spectra of molten  $\text{RbMnCl}_3$ . The smooth line is the best-fit curve calculated with a single Gaussian\*Lorentzian function.

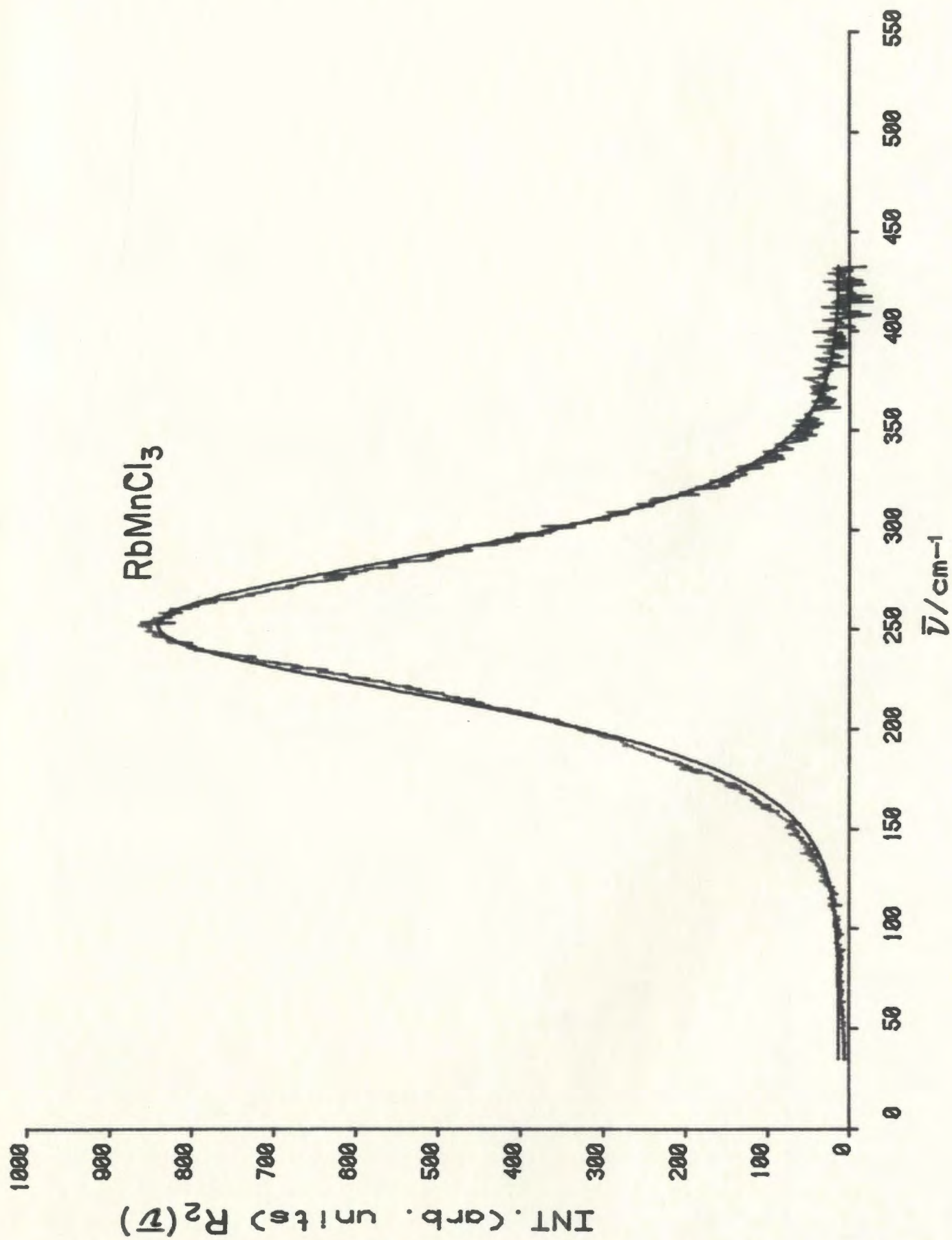




Figure 29. Isotropic Raman spectra of molten  $\text{Rb}_2\text{MnCl}_4$ . The smooth line is the best-fit curve calculated with a single Lorentzian function.

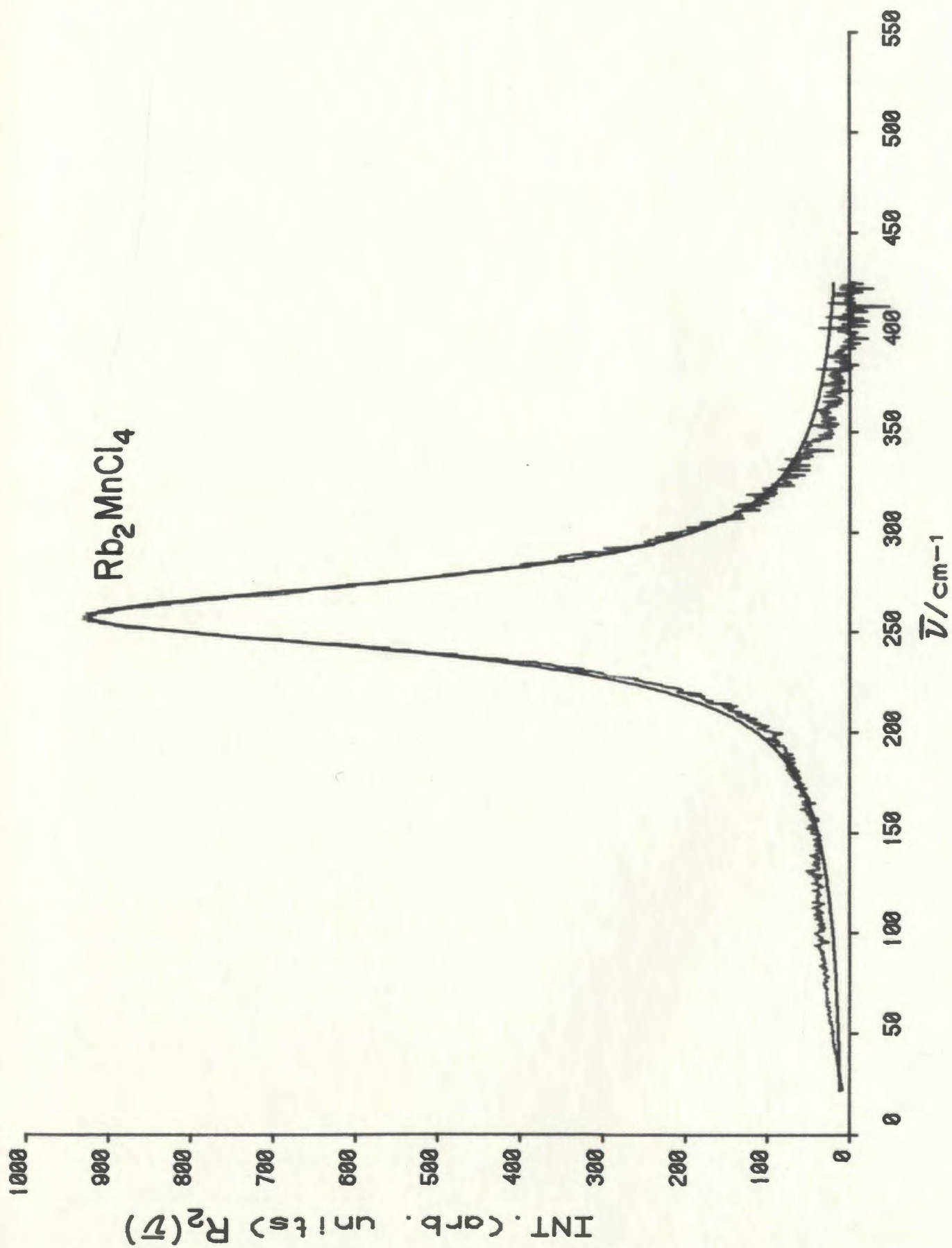


Figure 30. Isotropic Raman spectra of molten  $\text{RbCl}:\text{MnCl}_2$  (3:1).  
The smooth line is the best-fit curve calculated with  
a single Lorentzian function.



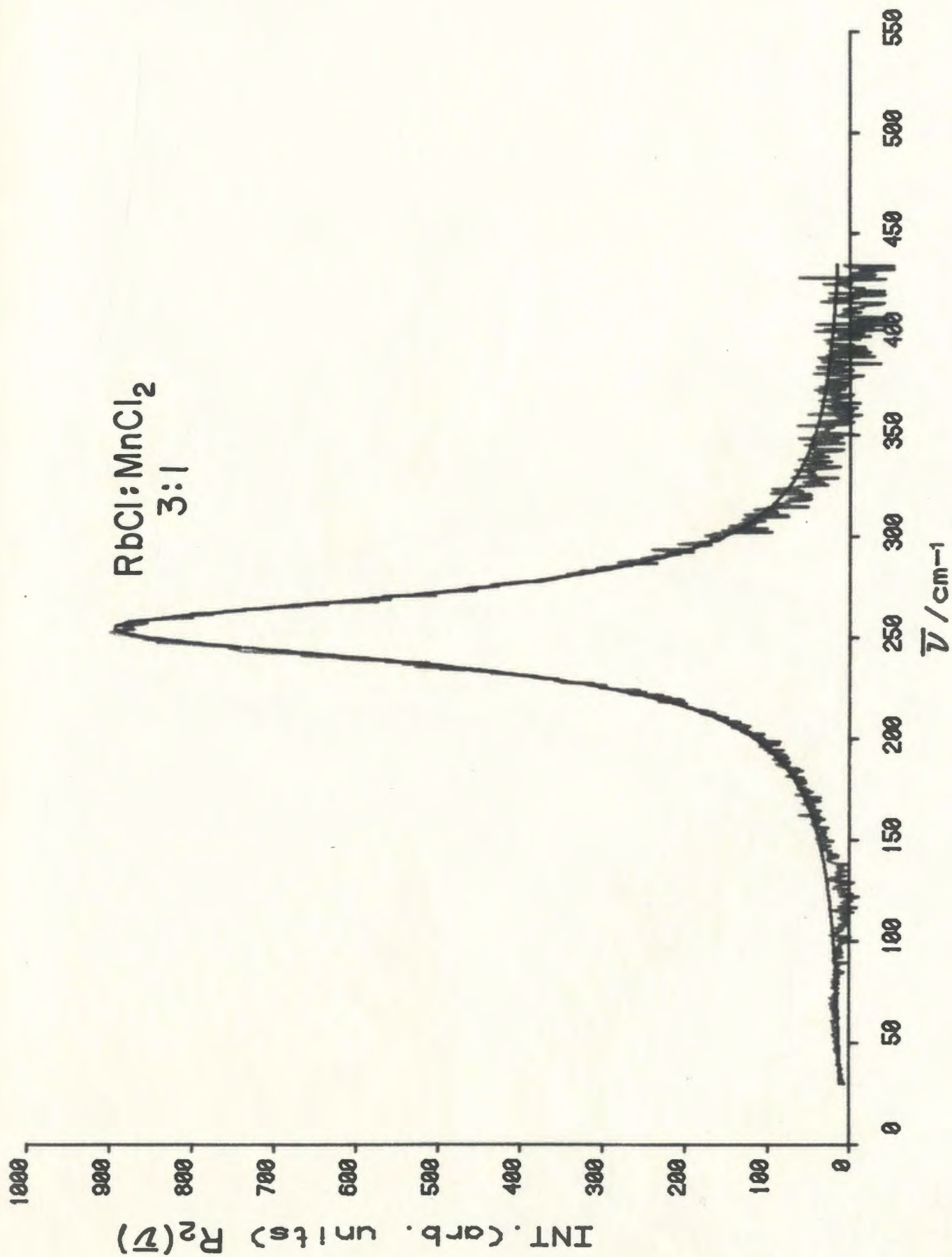
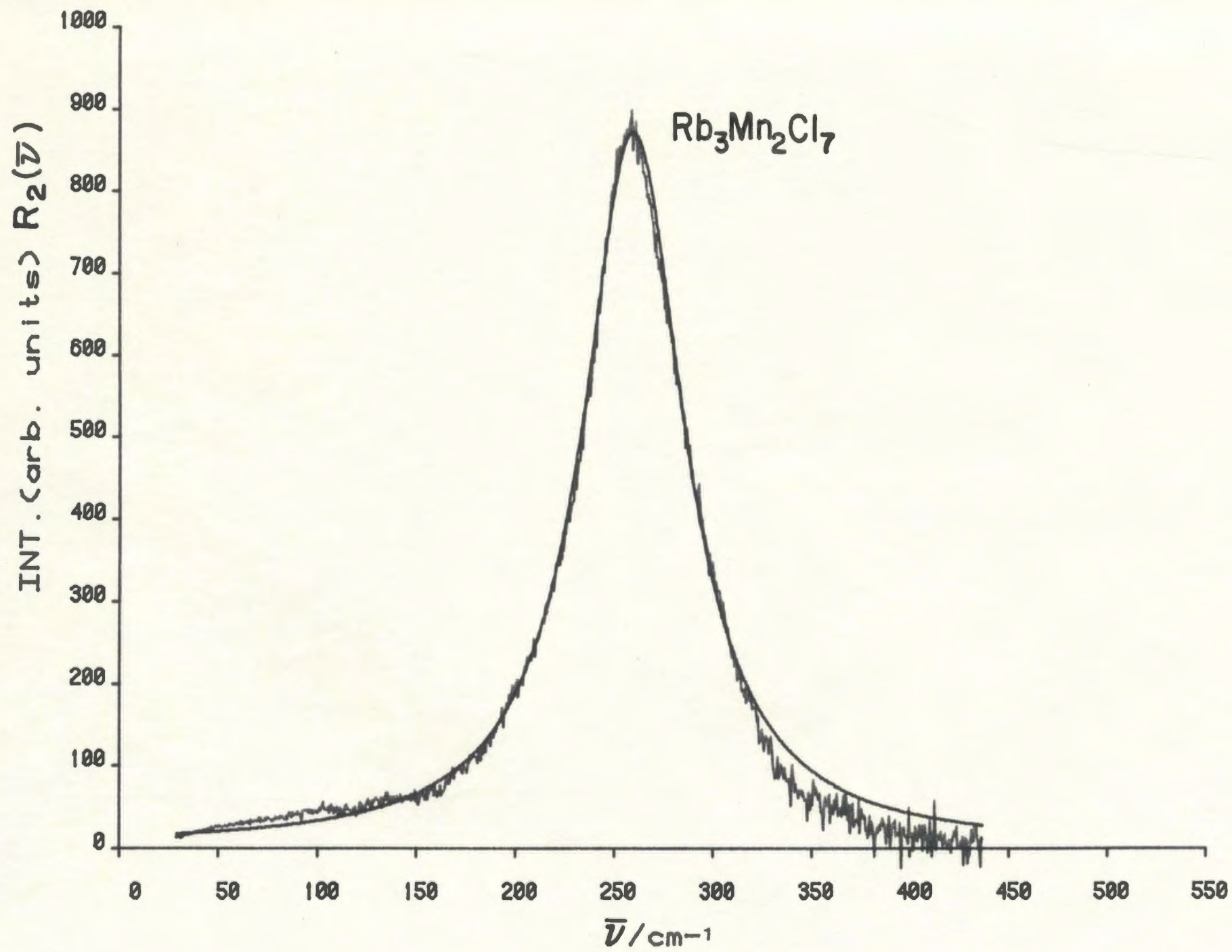


Figure 31. Isotropic Raman spectra of molten  $\text{Rb}_3\text{Mn}_2\text{Cl}_7$ . The smooth line is the best-fit curve calculated with a single Lorentzian function.





the existence of  $\text{MnCl}_4^{2-}$  as an isolated entities for melts with high KCl content or with corner sharing for melts with low KCl content. For  $\text{KCl} \cdot \text{XMnCl}_2$  melts ( $X = 0.2, 0.3, 0.4$ ). A previous Raman study<sup>19</sup> proposed the tetrahedral  $\text{MnCl}_4^{2-}$  ion as the predominant species in this concentration range, but pyramidal  $\text{MnCl}_3^-$  ion or  $\text{Mn}_2\text{Cl}_7^{3-}$  were also proposed in this composition range, whereas  $\text{MnCl}_6^{4-}$  ion was proposed in the concentration range ( $x = 0.9, 0.8, 0.67$ ) and small amount of  $\text{MnCl}_4^{2-}$  ion was also suggested.

It was reported<sup>19</sup> that the half band width of the totally symmetric mode increased with increased  $\text{MnCl}_2$  concentration and the effect attributed to sharing of Cl ion. The present results confirmed the increment in the half band width upon increasing  $\text{MnCl}_2$  mole fraction, see Table 22.

The polarized peak from the  $R_2(\bar{\nu})$  spectrum was fitted to Gaussian\*Lorentzian and Lorentzian functions. The results are shown in figures 37, 38, 39, 40 and 41 and tabulated in Table 22.

#### 4.2.4 $\text{MnCl}_2$ -NaCl Melts

The Raman spectra of  $\text{NaMnCl}_3$ ,  $\text{Na}_2\text{MnCl}_4$ ,  $\text{NaCl}:\text{MnCl}_2$  (3:1),  $\text{Na}_2\text{Mn}_3\text{Cl}_8$ ,  $\text{NaMn}_4\text{Cl}_9$ , and  $\text{Na}_6\text{MnCl}_8$  are shown in figures 42, 43, 44, 45, 46 and 47. One polarised peak was observed in each spectrum and assigned to the symmetric mode ( $\nu_1$ ). The  $\nu_2$  and  $\nu_4$  modes were observed in the region  $70\text{-}140\text{ cm}^{-1}$ . The antisymmetric mode  $\nu_3$  of the tetrahedral ion is usually weak in the Raman spectrum and appear around  $\sim 300\text{ cm}^{-1}$ . The spectra indicate the presence of tetrahedral species in the melts. The half band width of the symmetric mode  $\nu_1$  increased with increased  $\text{MnCl}_2$  concentration, see Table 23.

Table 22. Summary of results of curve resolution analysis for  $\text{MnCl}_2\text{-KCl}$  Melts.

Compound	Frequency ( $\text{cm}^{-1}$ )	Intensity	Half band width ( $\text{cm}^{-1}$ )	Function
$\text{K}_4\text{MnCl}_6$	256.0	887	45.9	L
$\text{KCl:MnCl}_2$ (3:1)	255.7	801	48.2	L
$\text{KCl:MnCl}_2$ (2:1)	255.0	850	51.4	L
$\text{K}_3\text{Mn}_2\text{Cl}_7$	258.4	879	63.6	L
$\text{KMnCl}_3$	258.9	770	86.7	G * L

G: Gaussian, L: Lorentzian

Figure 32. Raman spectra of molten  $\text{KMnCl}_3$  at 816 K,  $I_{||}$   
and  $I_{\perp}$ .



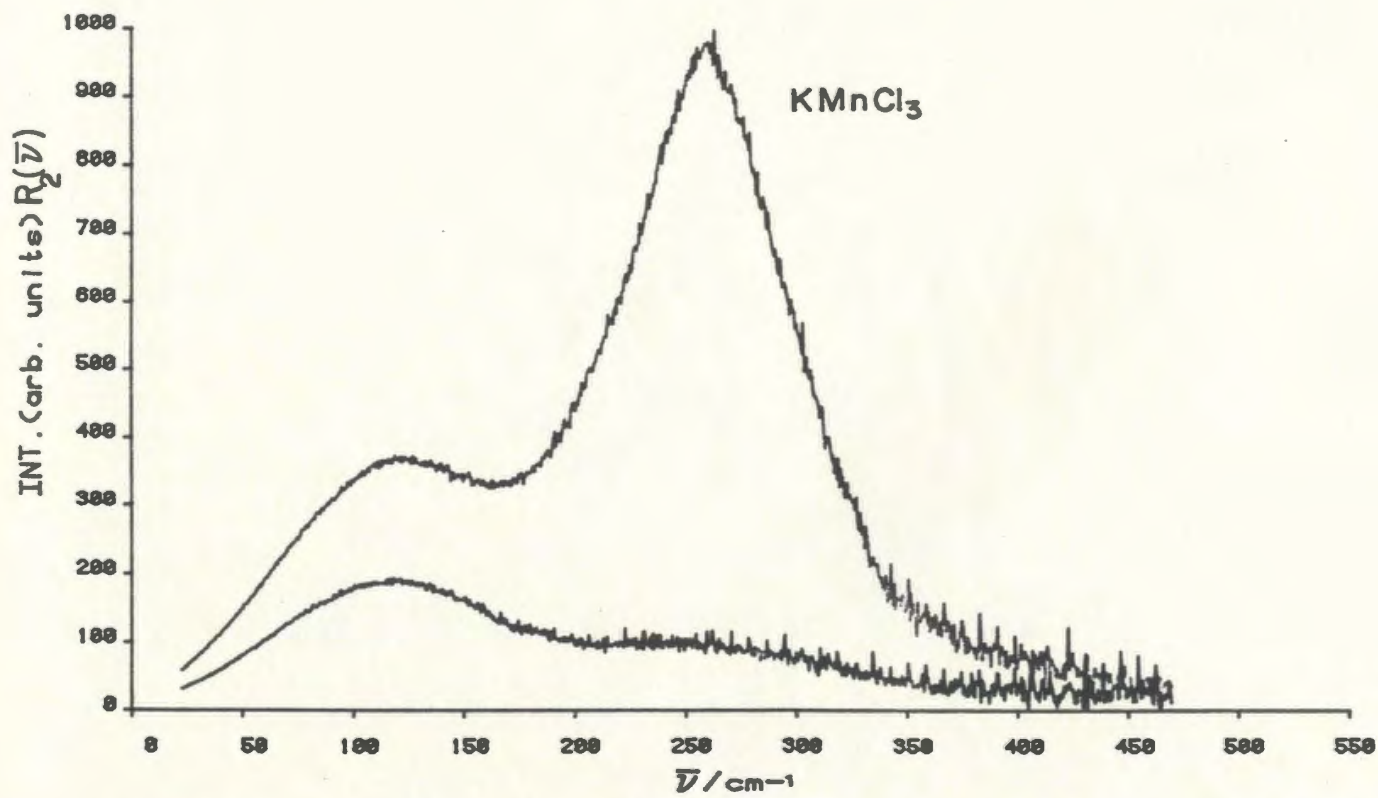
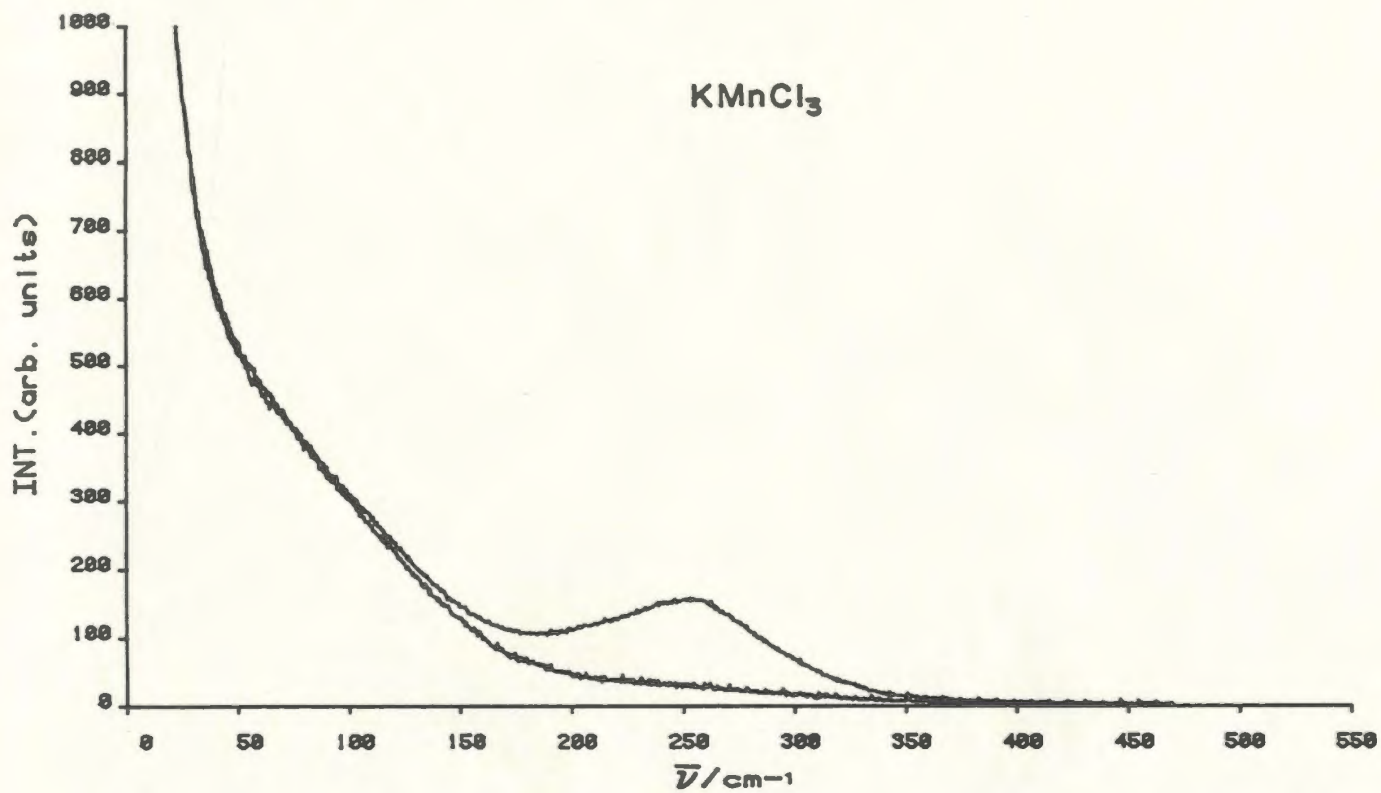


Figure 33. Raman spectra of molten  $\text{KCl}:\text{MnCl}_2$  (2:1) at 882 K,  $I_{||}$  and  $I_{\perp}$ .

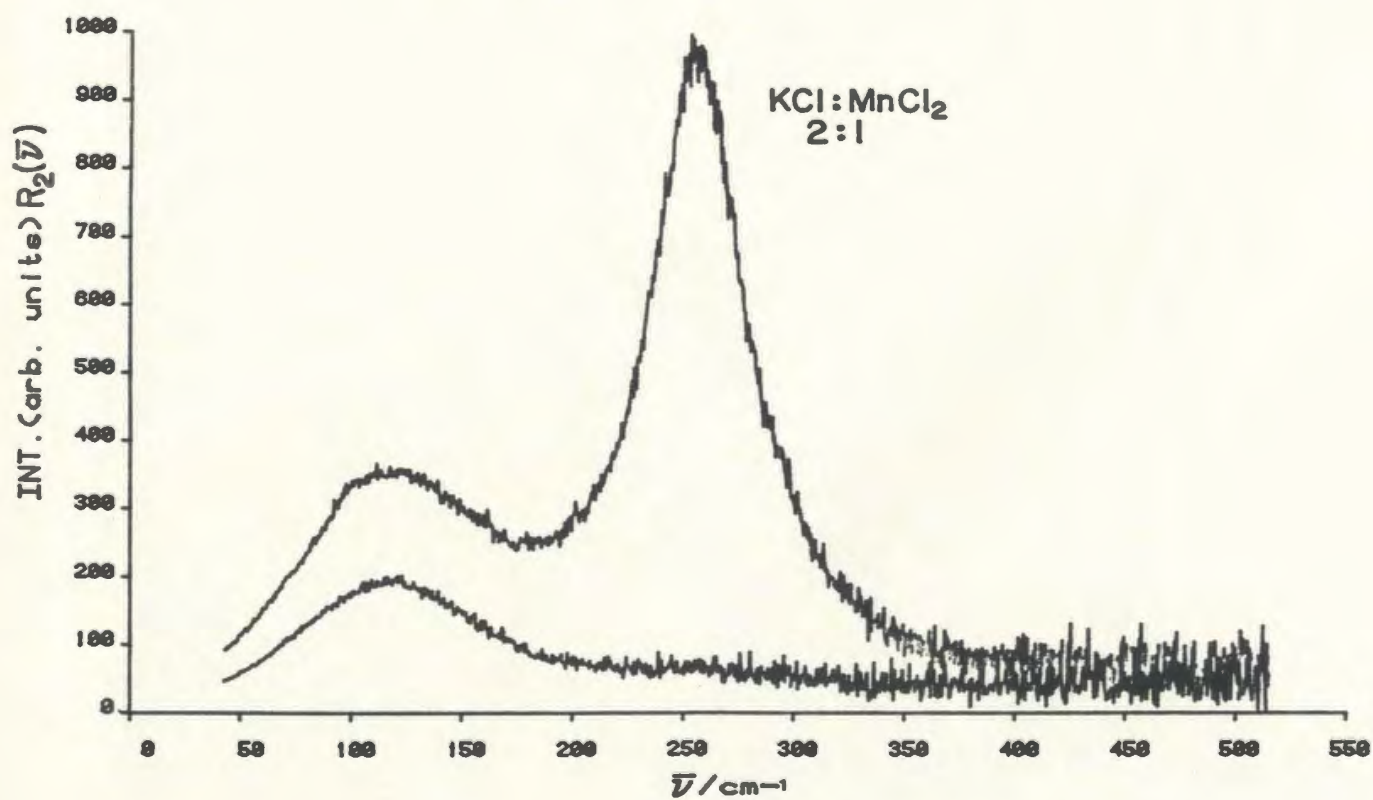
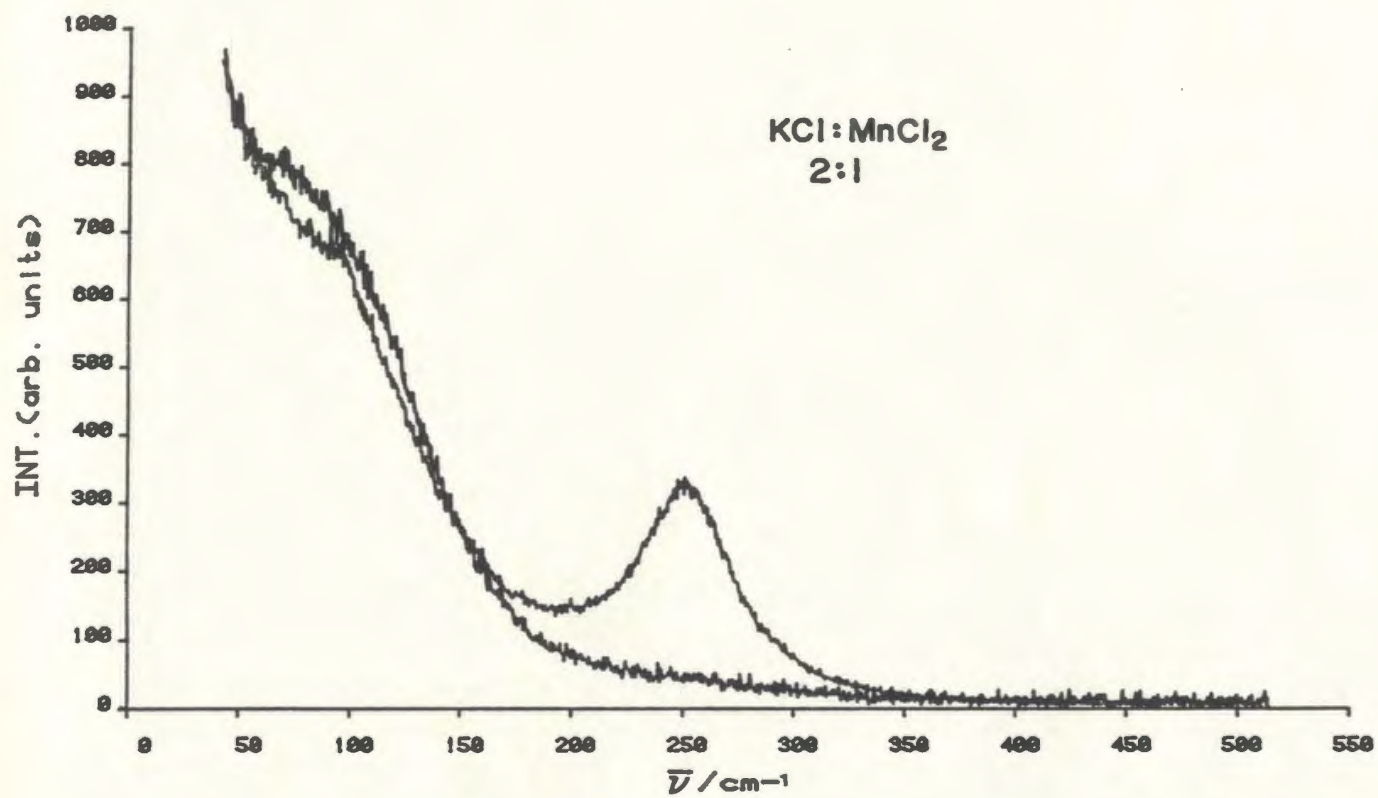




Figure 34. Raman spectra of molten  $\text{KCl}:\text{MnCl}_2$  (3:1) at  
882 K,  $I_{||}$  and  $I_{\perp}$ .

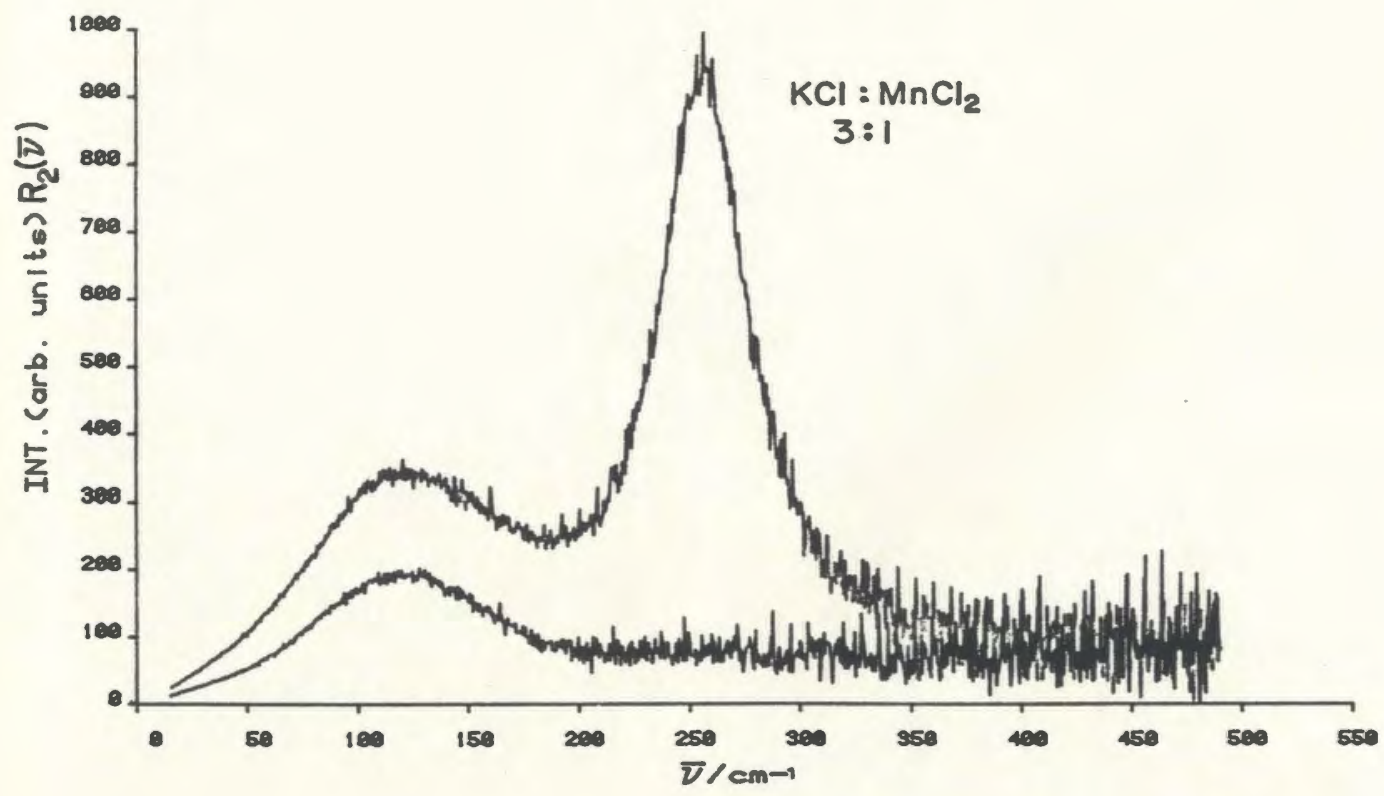
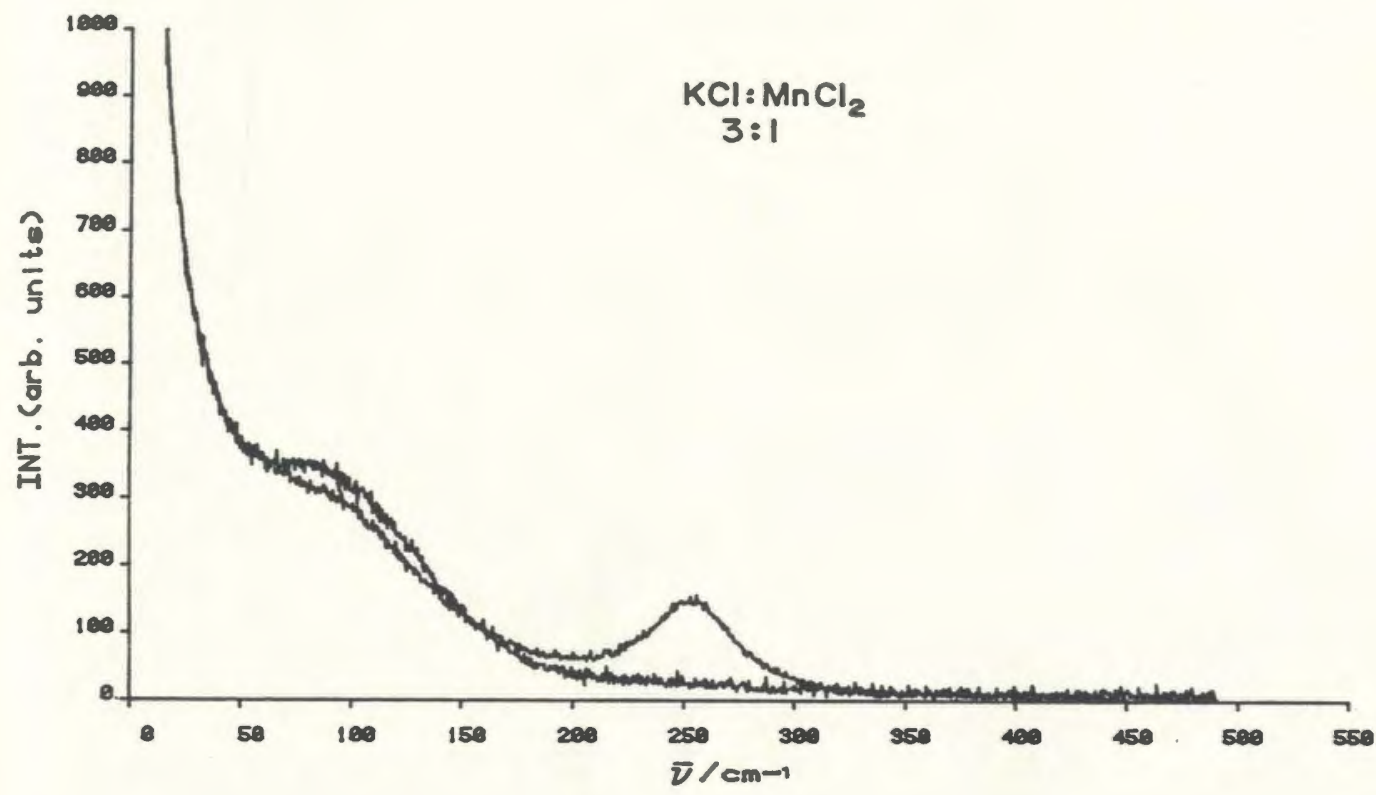


Figure 35. Raman spectra of molten  $\text{K}_3\text{Mn}_2\text{Cl}_7$  at 794 K,  $I_{||}$   
and  $I_{\perp}$ .



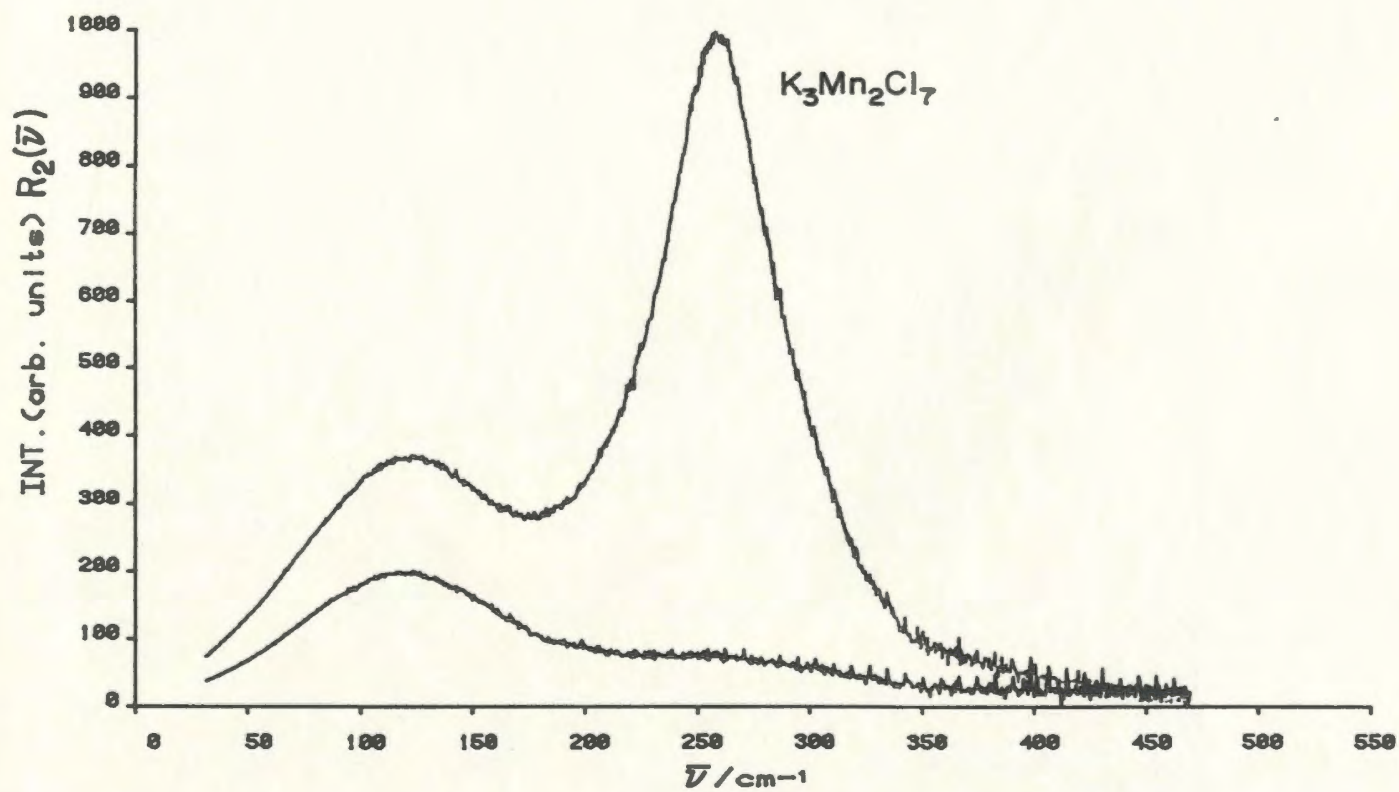
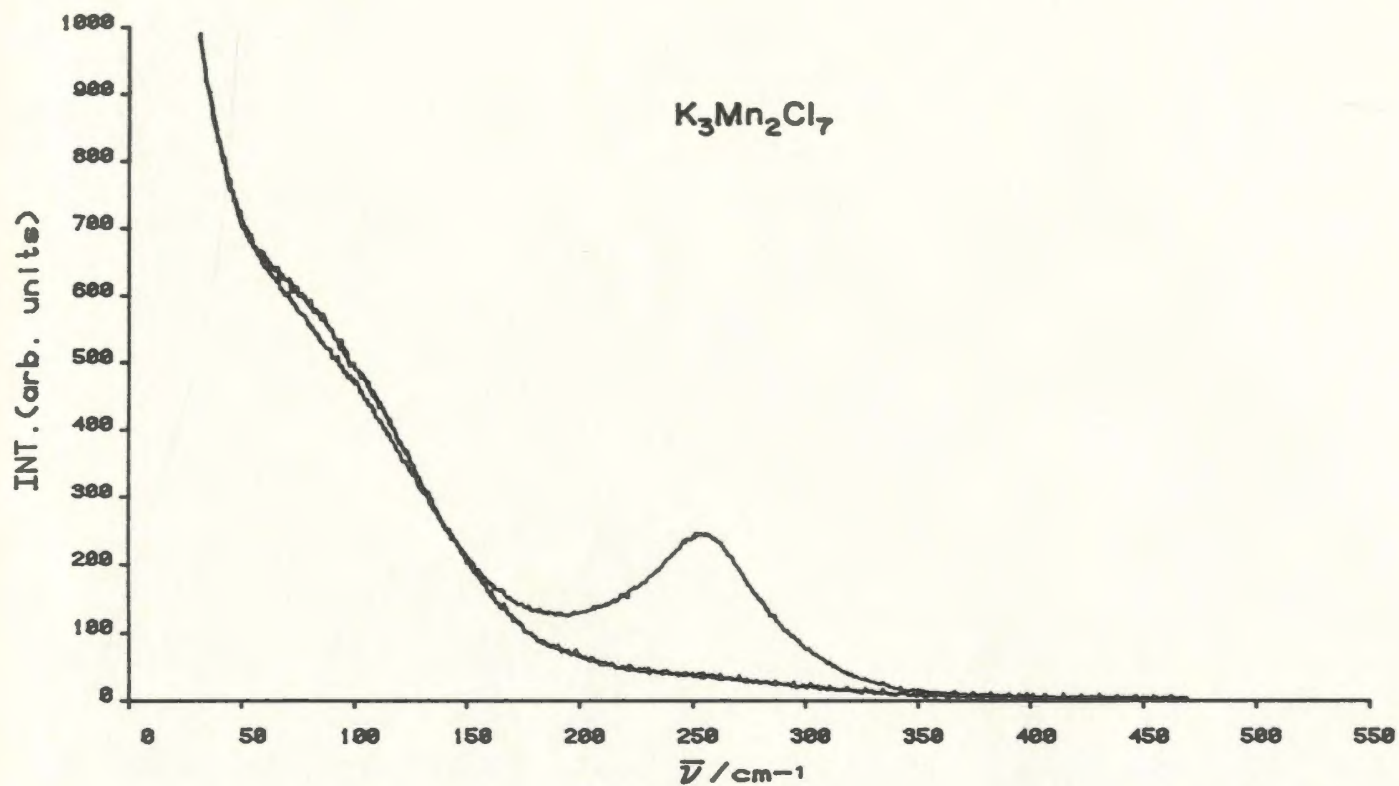


Figure 36. Raman spectra of molten  $\text{K}_4\text{MnCl}_6$  at 816 K,  $I_{||}$   
and  $I_{\perp}$ .

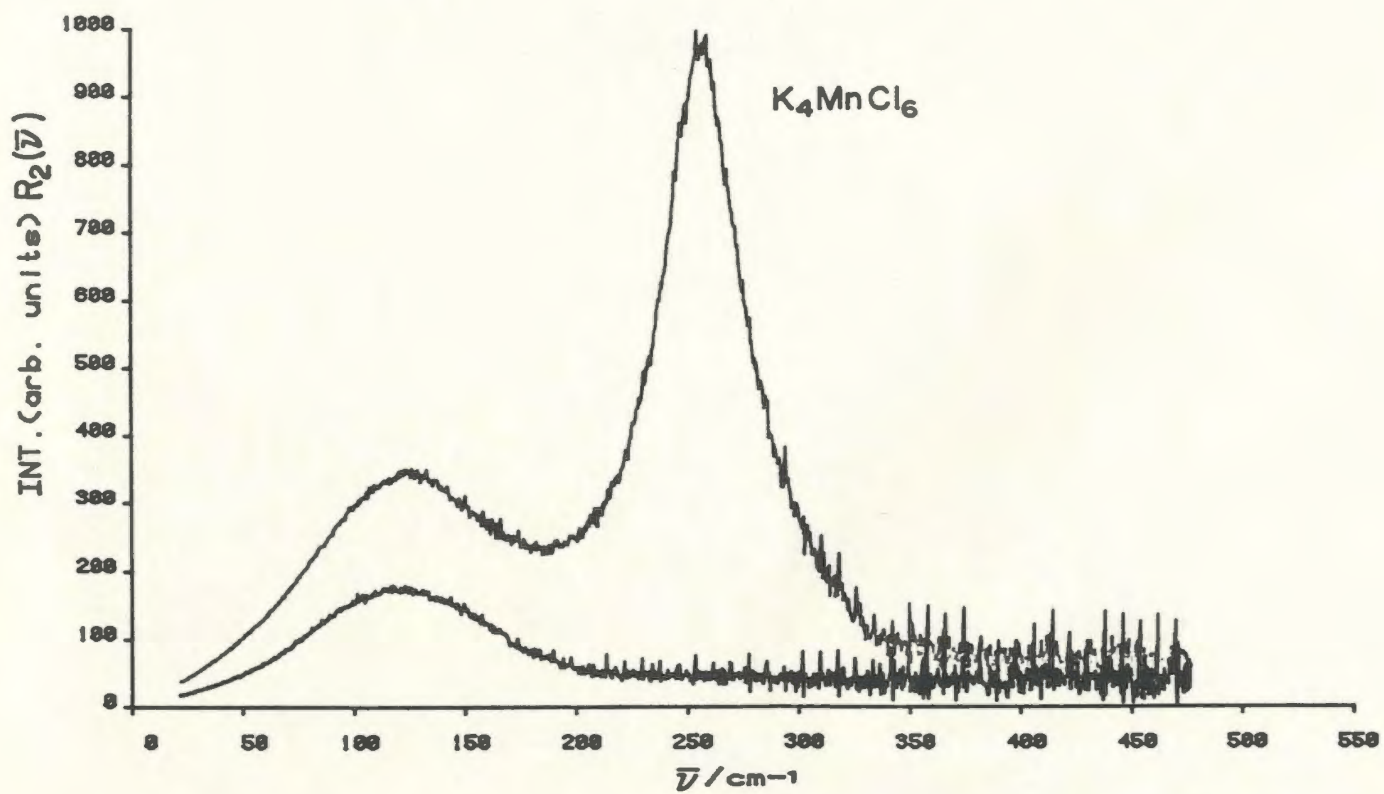
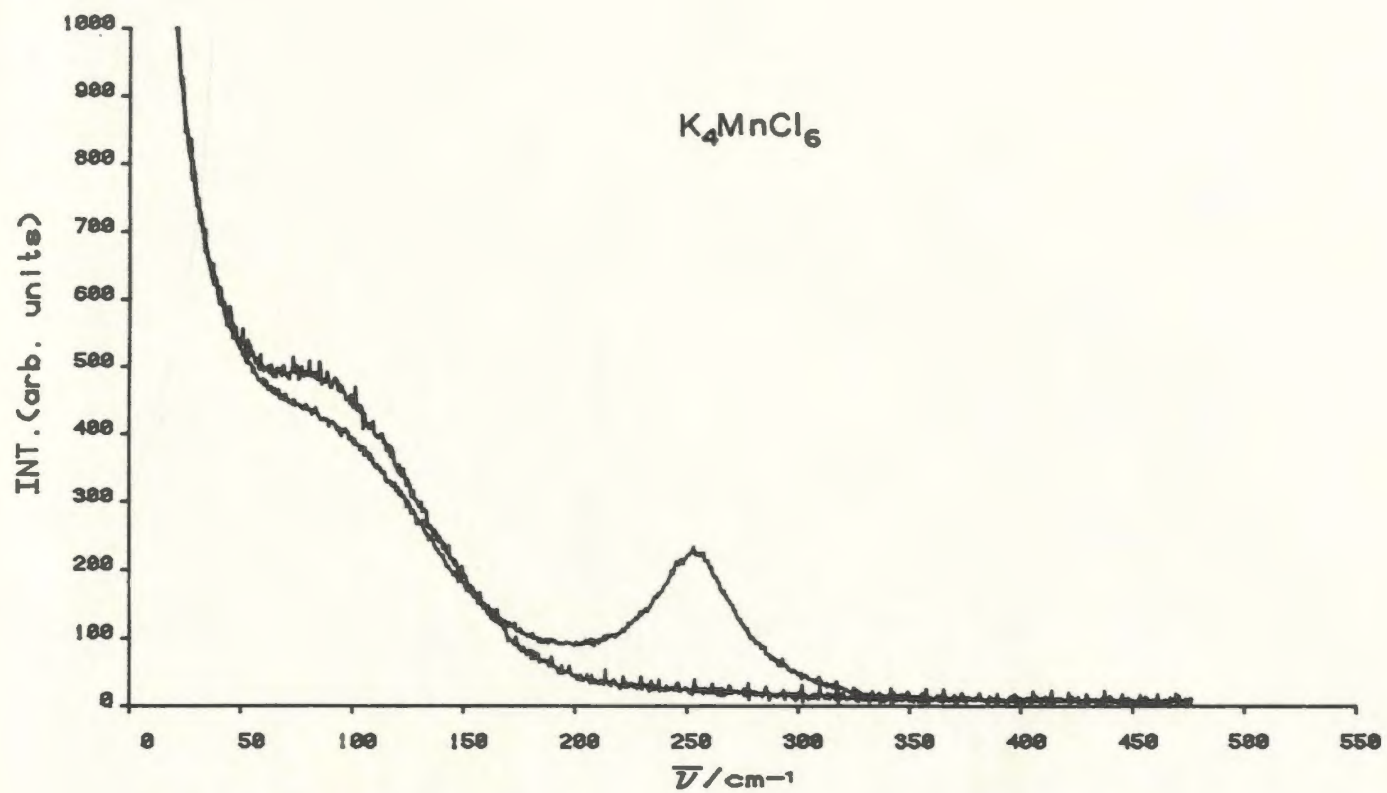




Figure 37. Isotropic Raman spectra of molten  $\text{KMnCl}_3$ . The smooth line is the best-fit curve calculated with a single Gaussian\*Lorentzian function.

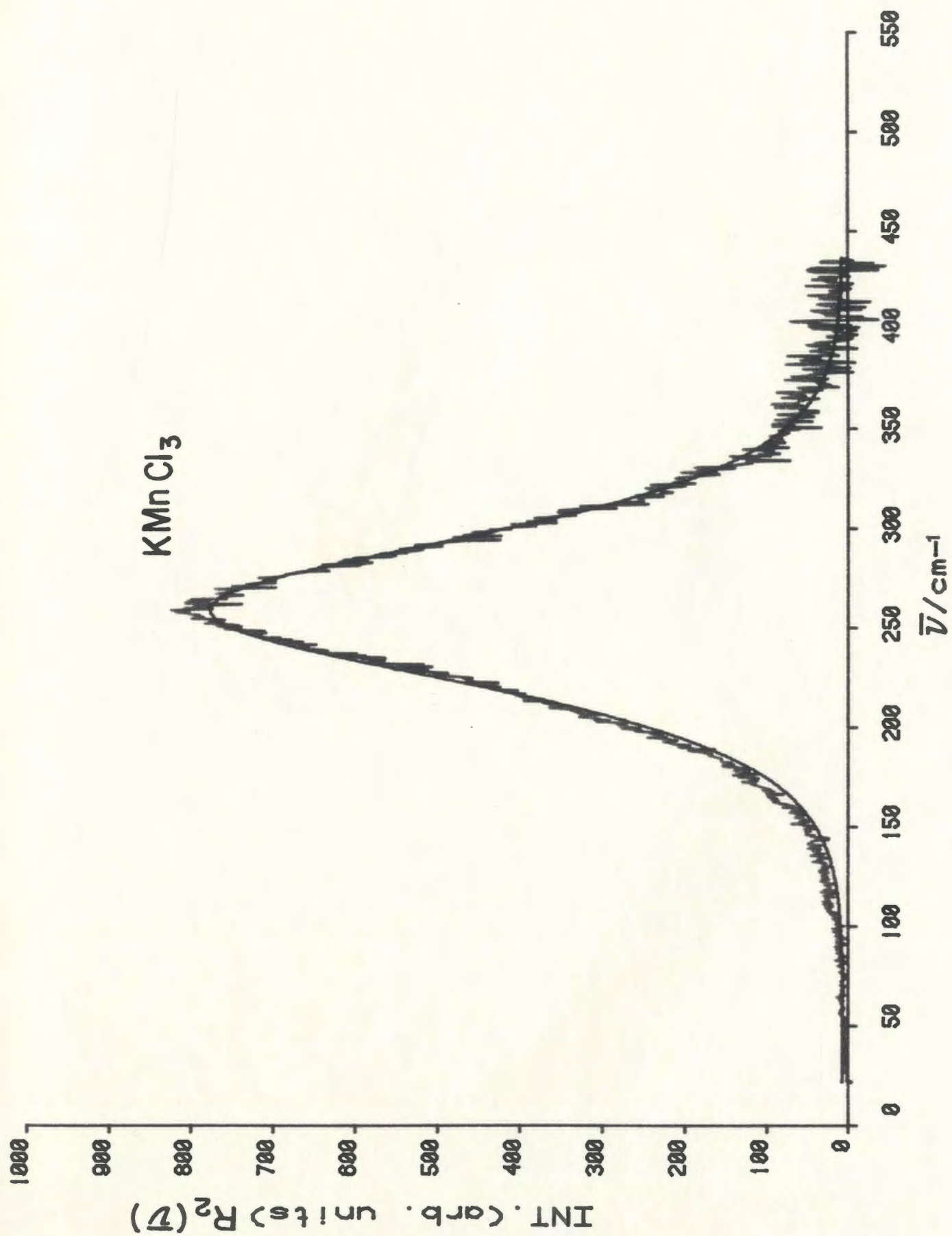


Figure 38. Isotropic Raman spectra of molten  $\text{KCl:MnCl}_2$  (2:1).  
The smooth line is the best-fit curve calculated with  
a single Lorentzian function.



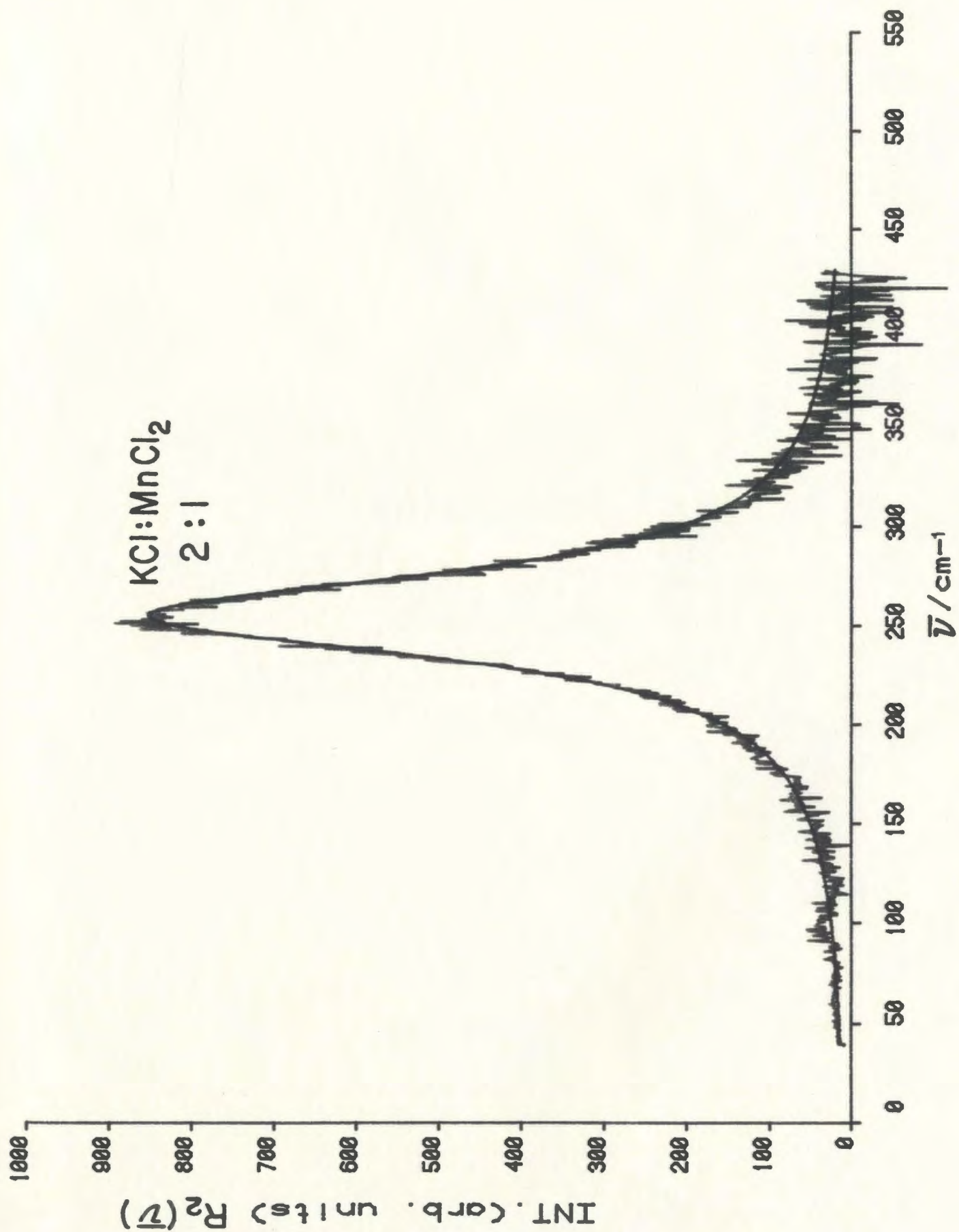


Figure 39. Isotropic Raman spectra of molten  $\text{KCl:MnCl}_2$  (3:1).  
The smooth line is the best-fit curve calculated with  
a single Lorentzian function.

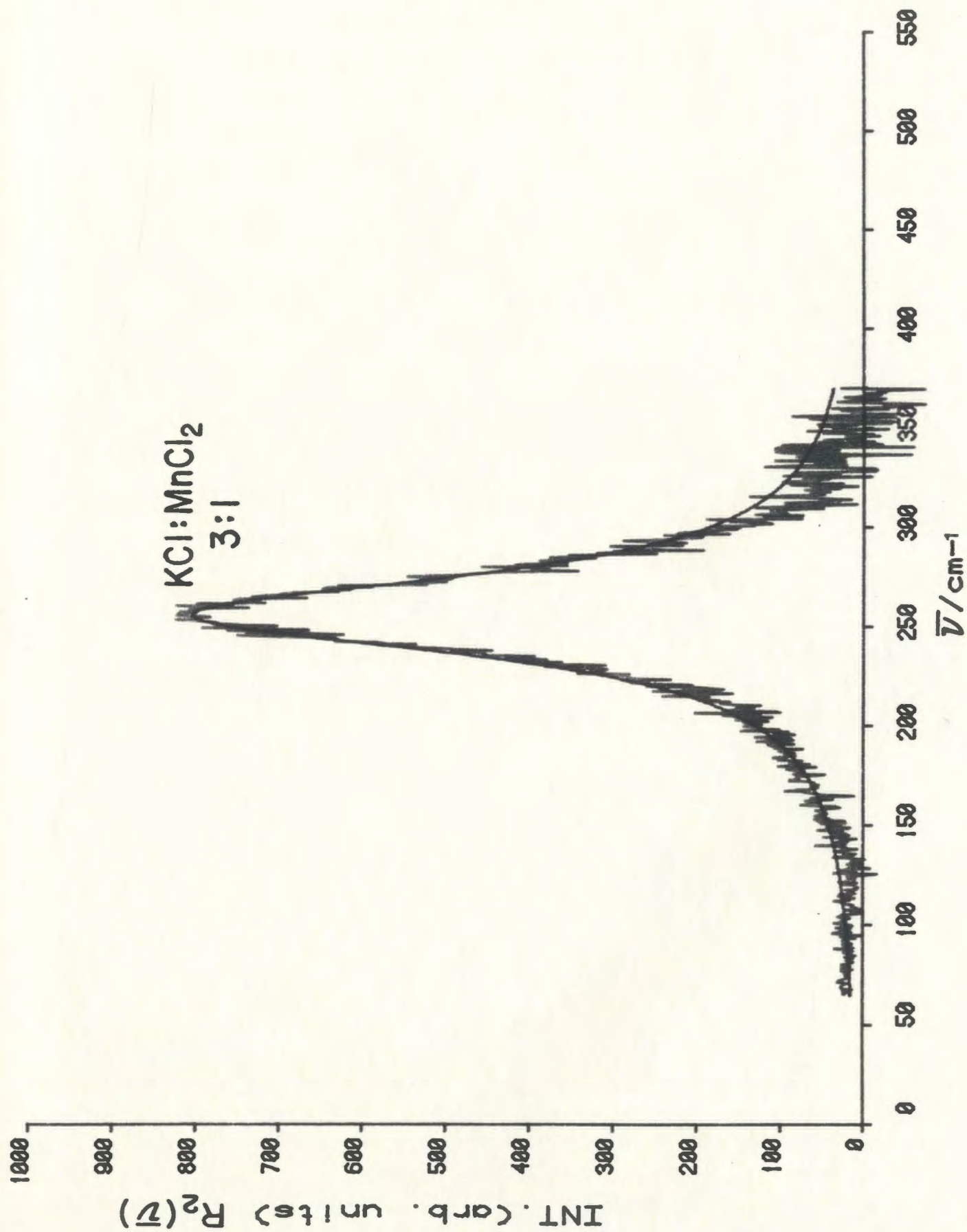




Figure 40. Isotropic Raman spectra of molten  $K_3Mn_2Cl_7$ . The smooth line is the best-fit curve calculated with a single Lorentzian function.

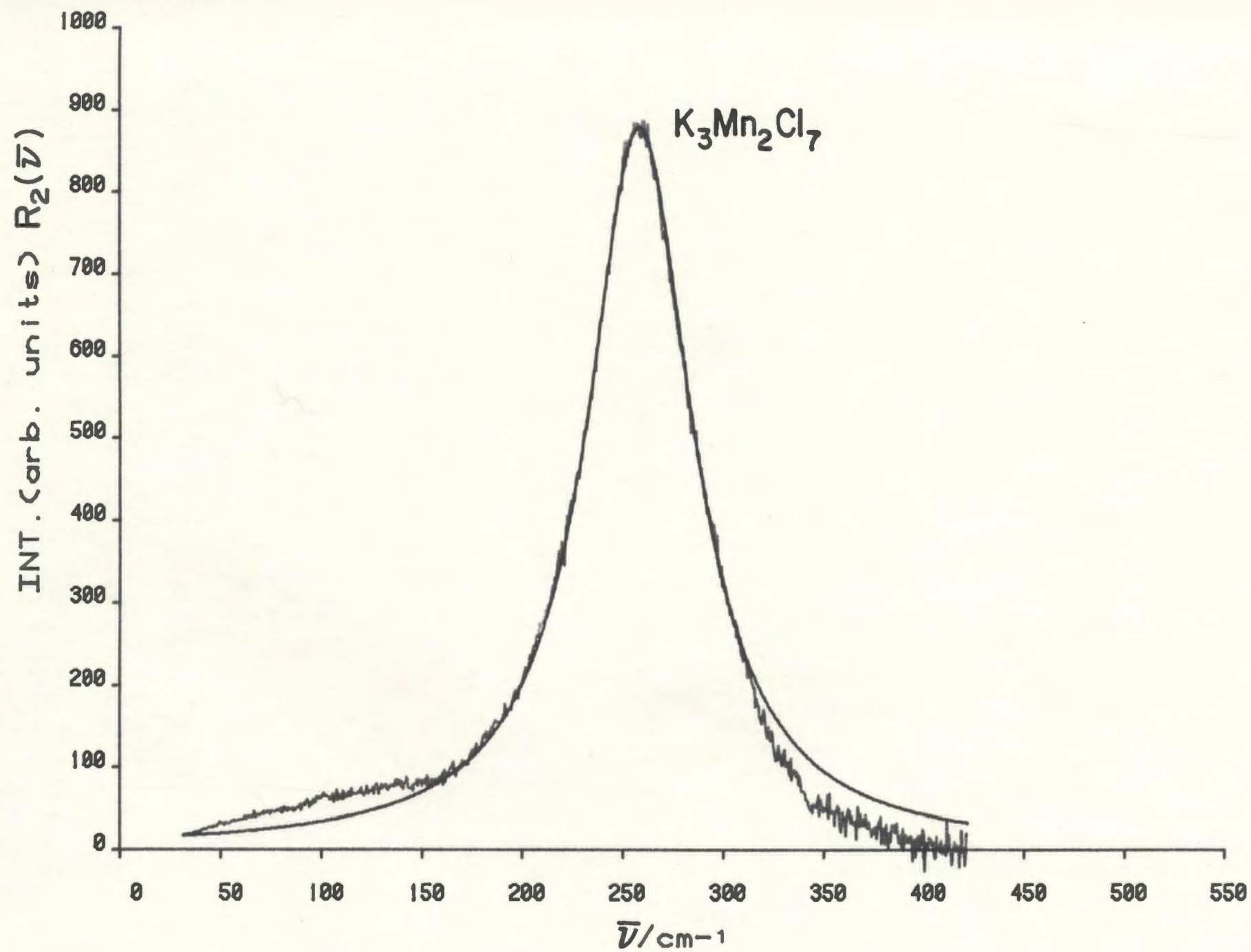


Figure 41. Isotropic Raman spectra of molten  $K_4MnCl_6$ . The smooth line is the best-fit curve calculated with a single Lorentzian function.



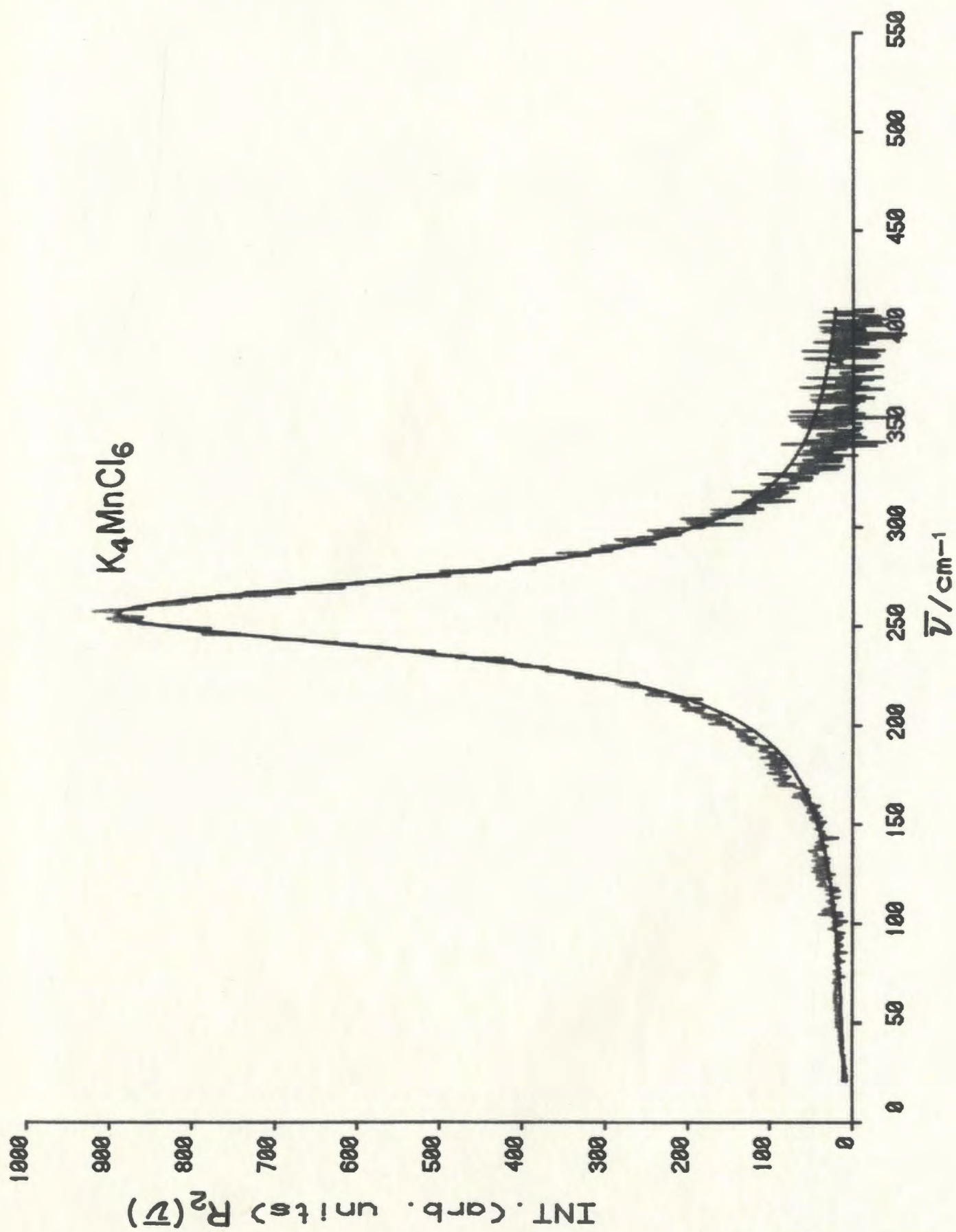


Table 23. Summary of results of curve resolution analysis for  $\text{MnCl}_2\text{-NaCl}$  Melts.

Compound	Frequency ( $\text{cm}^{-1}$ )	Intensity	Half band width ( $\text{cm}^{-1}$ )	Function
$\text{Na}_6\text{MnCl}_8$	255.6	832	77.6	G * L
$\text{NaCl:MnCl}_2$ (3:1)	254.4	819	79.4	G * L
$\text{Na}_2\text{MnCl}_4$	257.9	762	82.0	G * L
$\text{NaMnCl}_3$	253.3	699	92.3	G * L
$\text{Na}_2\text{Mn}_3\text{Cl}_8$	249.3	665	111.2	G * L
$\text{NaMn}_4\text{Cl}_9$	244.1	757	129.5	G * L

G: Gaussian, L: Lorentzian

Figure 42. Raman spectra of molten  $\text{NaMnCl}_3$  at 773 K,  $I_{||}$   
and  $I_{\perp}$ .



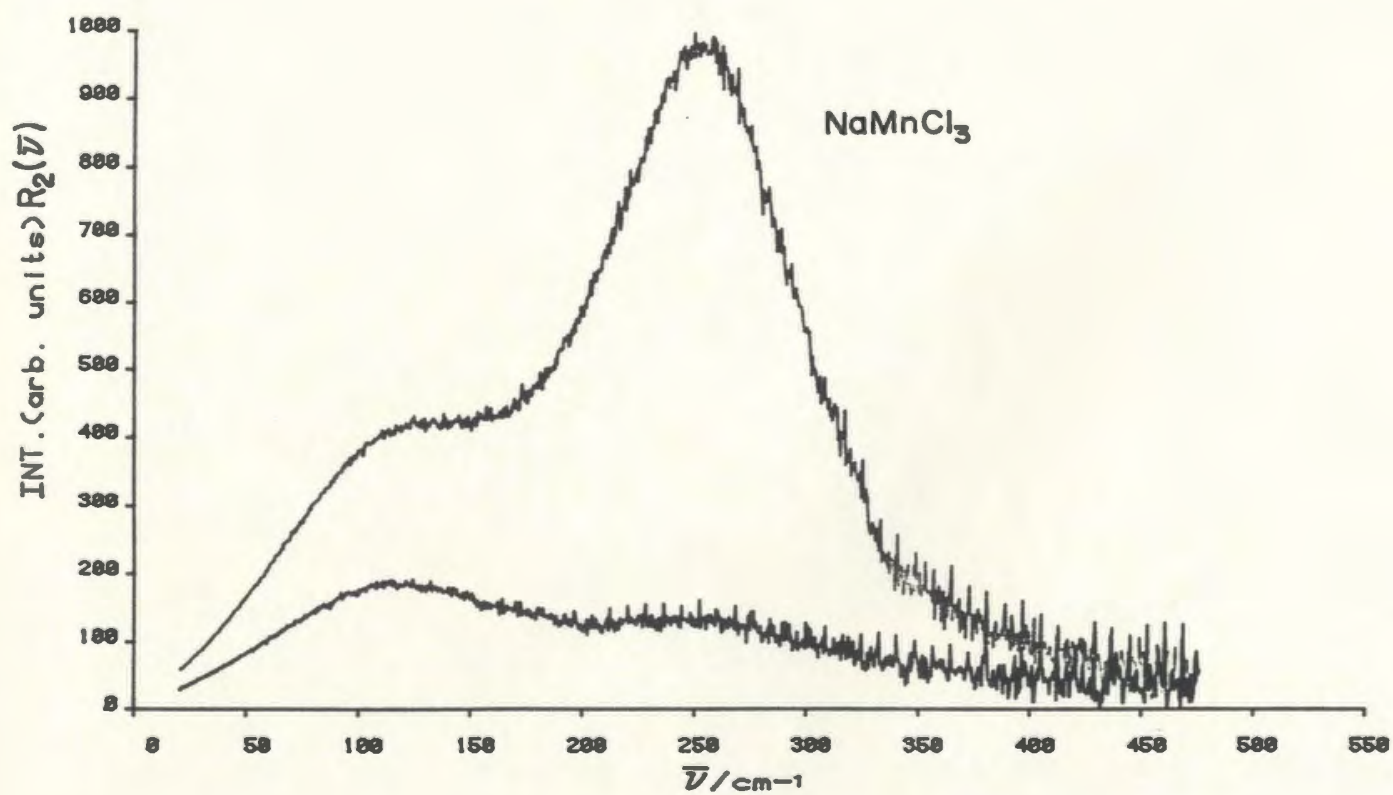
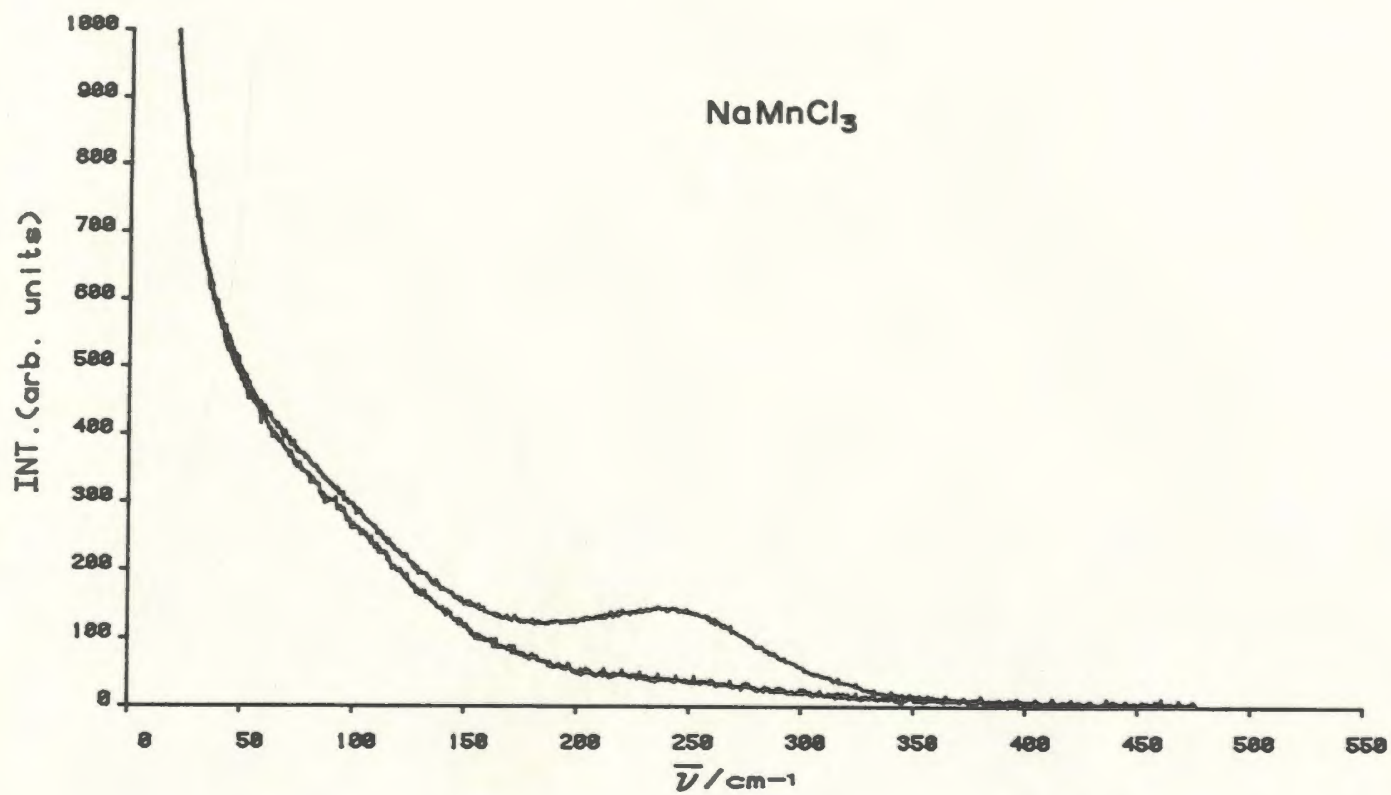


Figure 43. Raman spectra of molten  $\text{Na}_2\text{MnCl}_4$  at 794 K,  $I_{||}$   
and  $I_{\perp}$ .

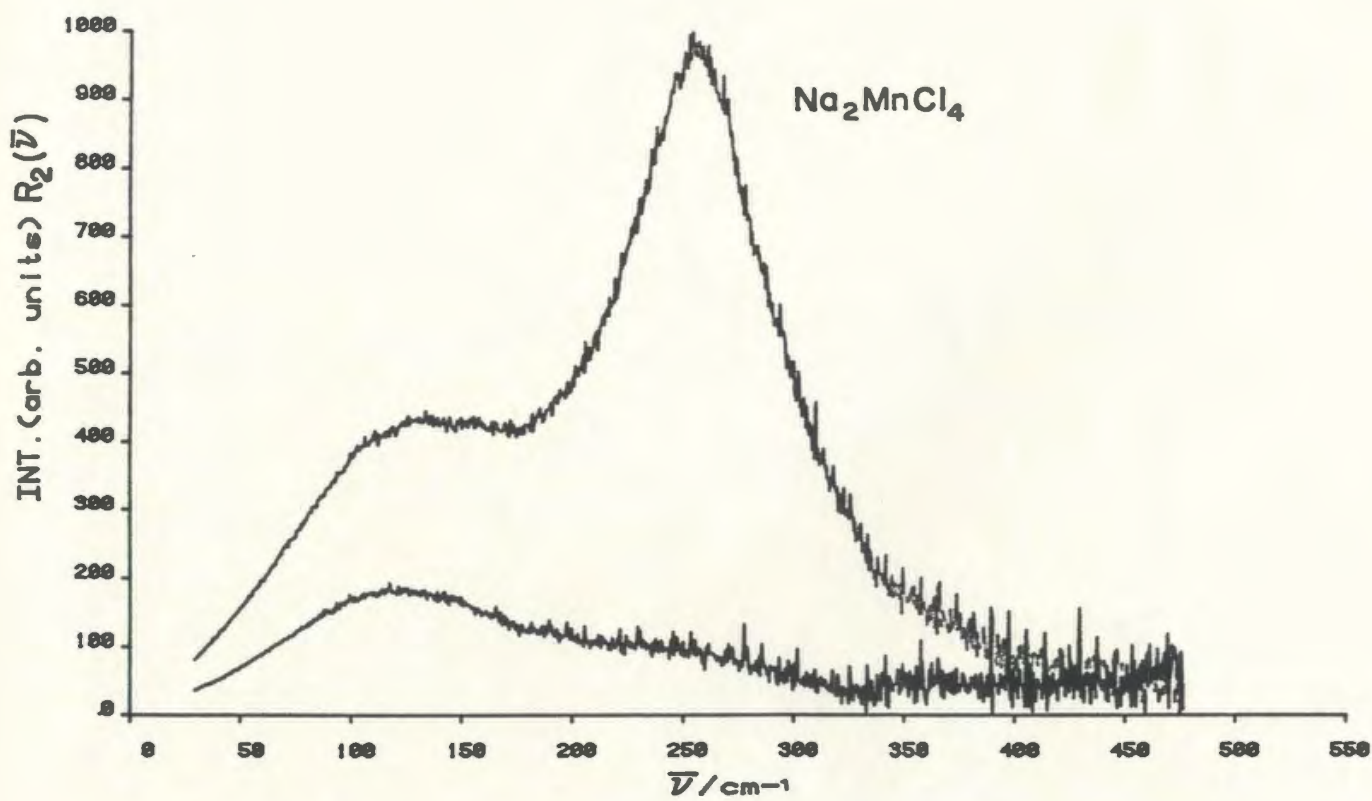
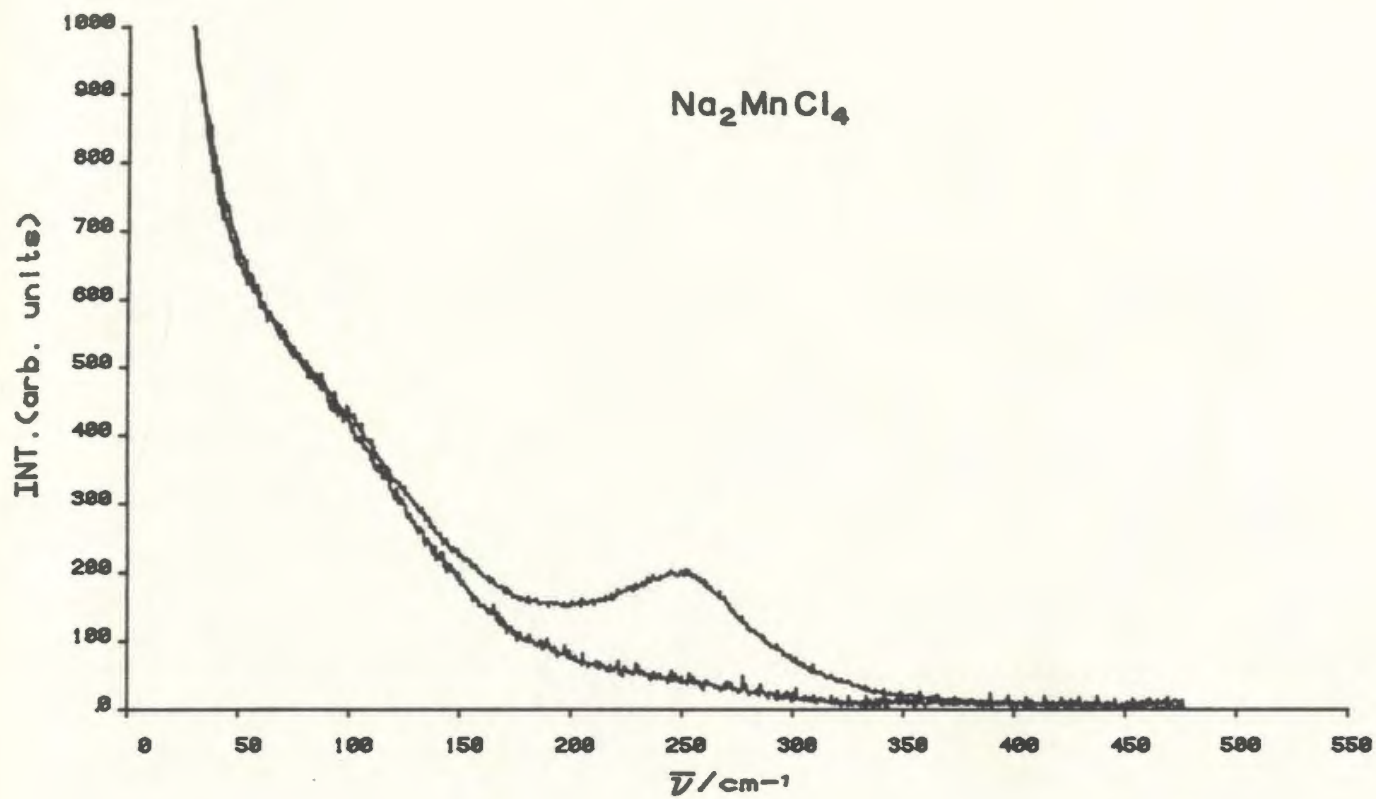




Figure 44. Raman spectra of molten  $\text{NaCl:MnCl}_2$  (3:1) at 973 K,  $I_{||}$  and  $I_{\perp}$ .

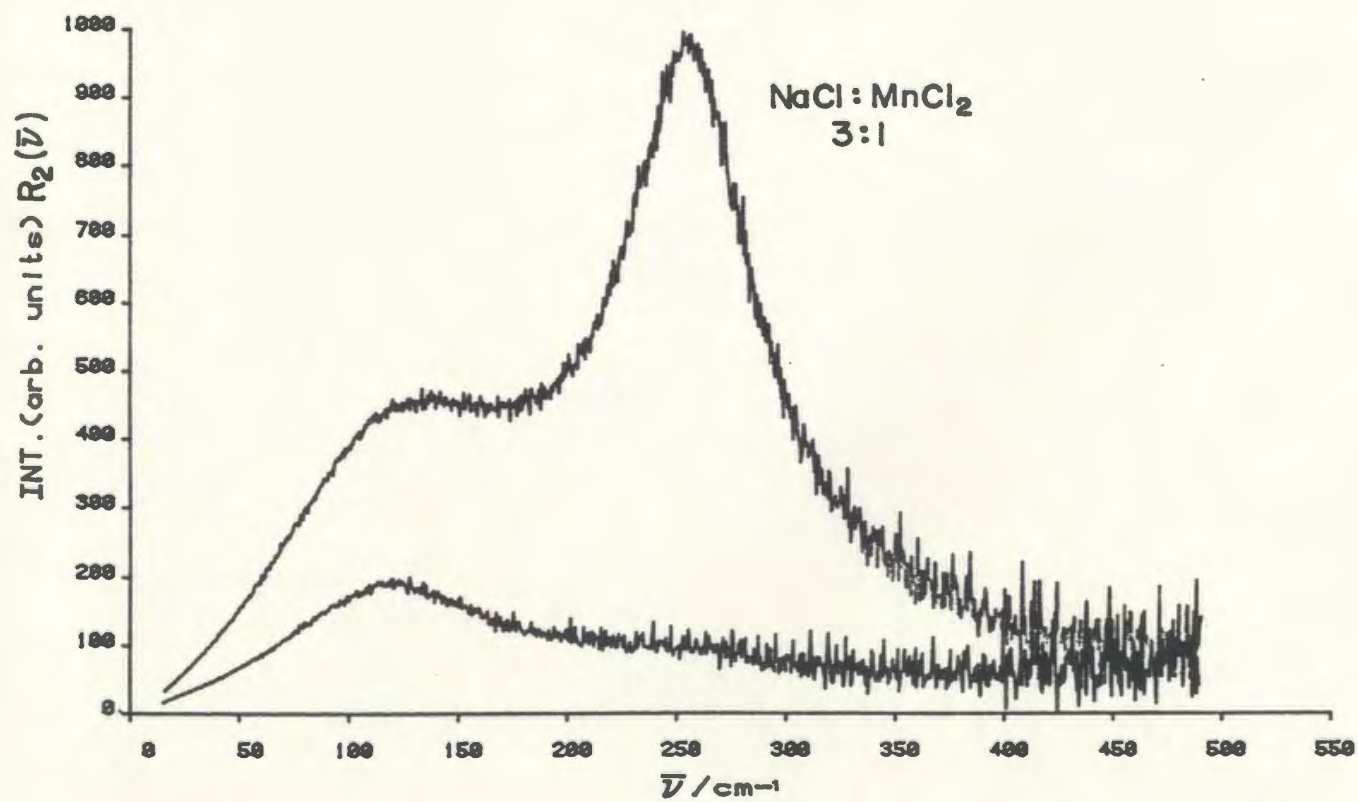
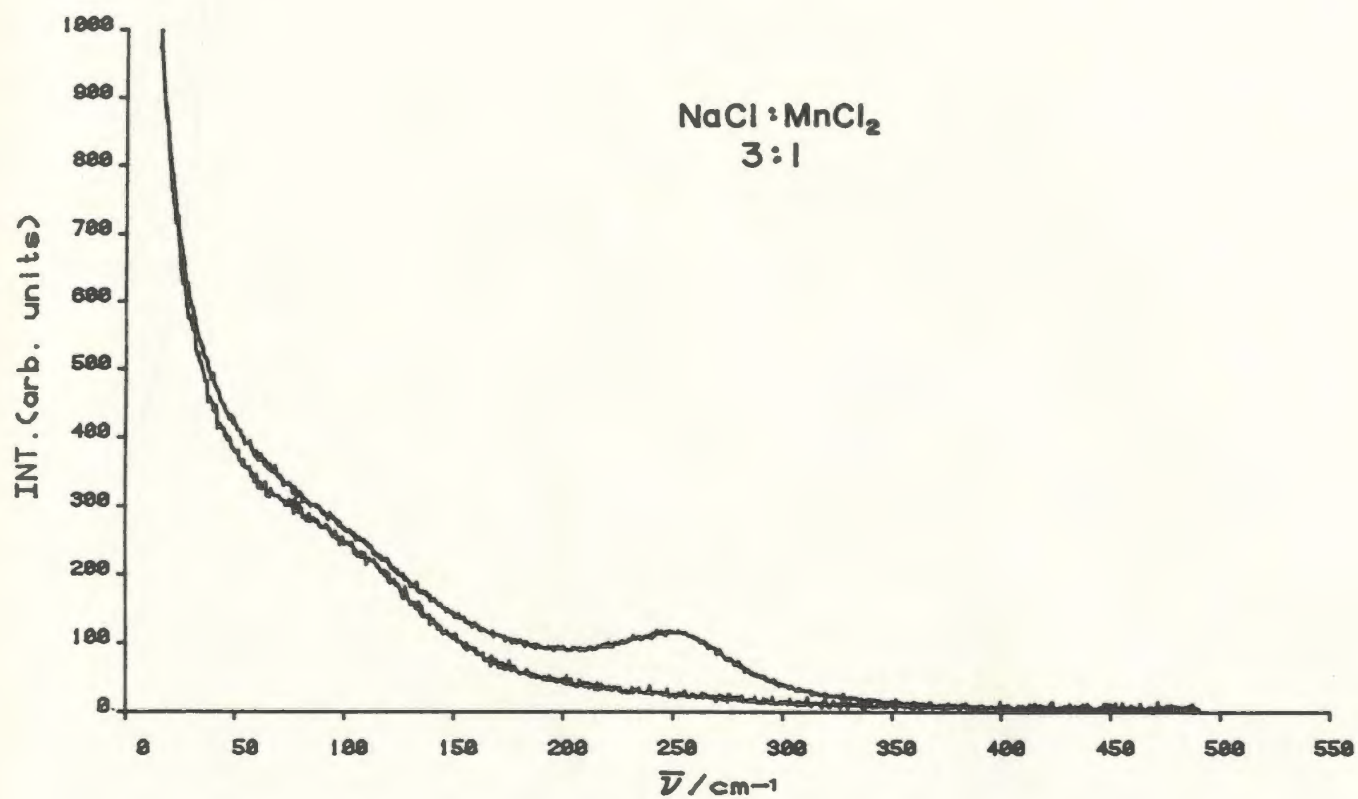


Figure 45. Raman spectra of molten  $\text{Na}_2\text{Mn}_3\text{Cl}_8$  at 816 K,

$I_{||}$  and  $I_{\perp}$ .



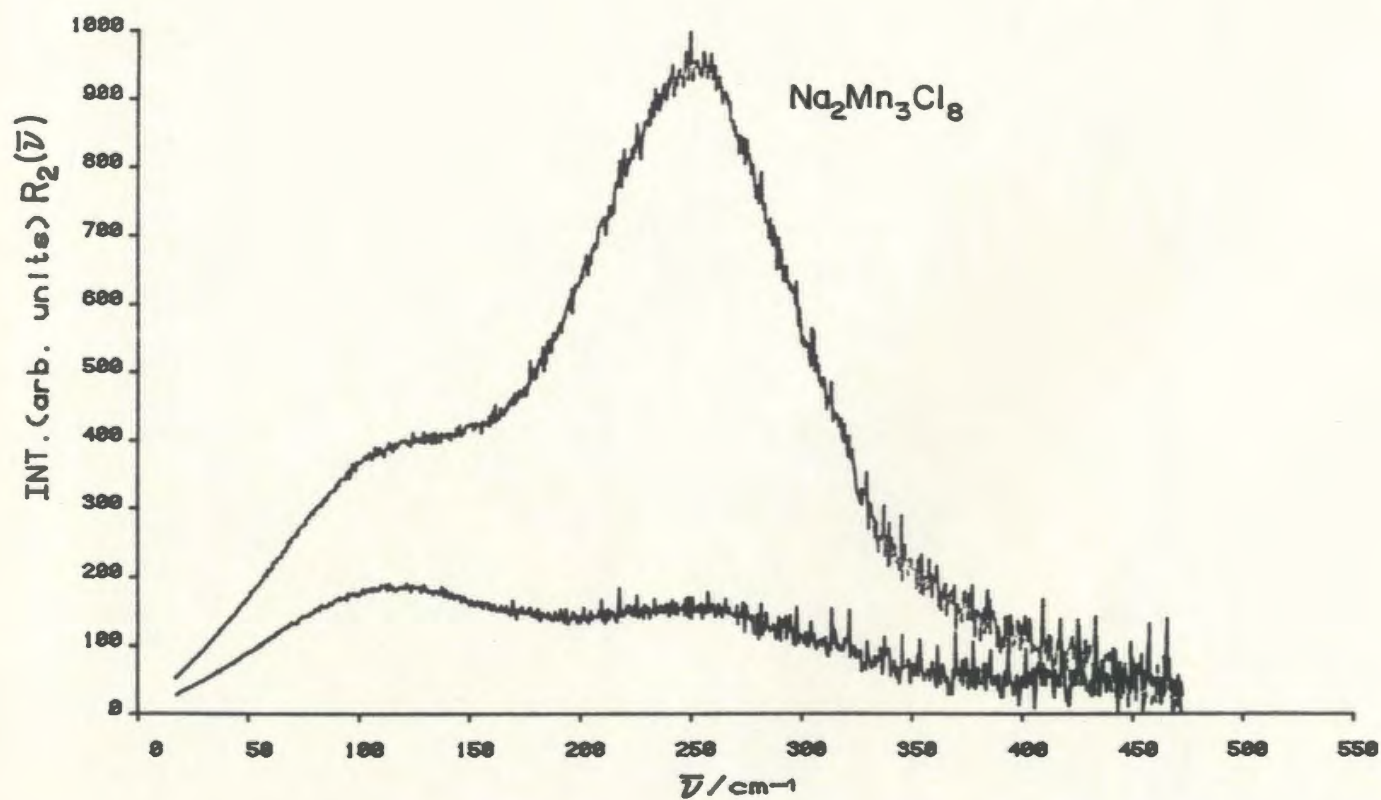
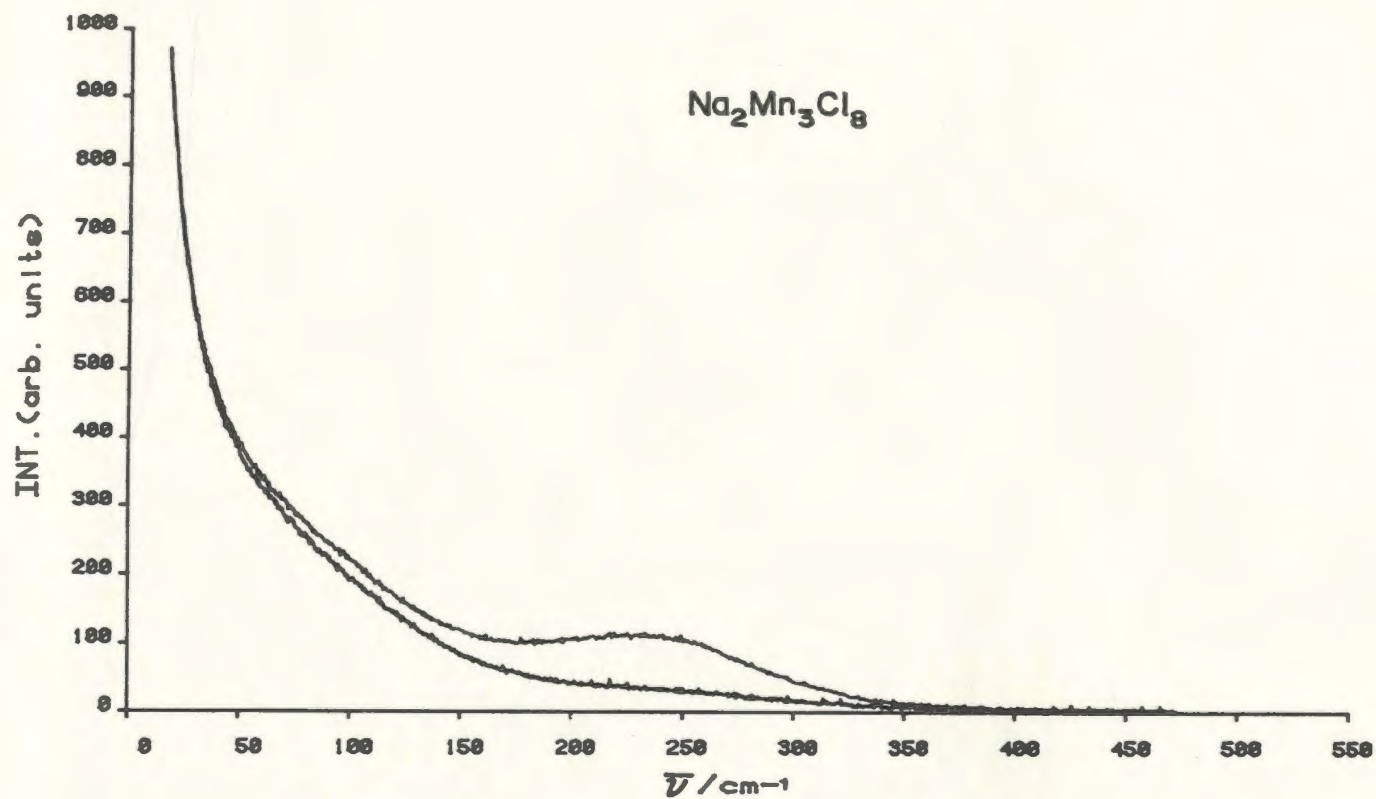


Figure 46. Raman spectra of molten  $\text{NaMn}_4\text{Cl}_9$  at 937 K,  $I_{||}$   
and  $I_{\perp}$ .

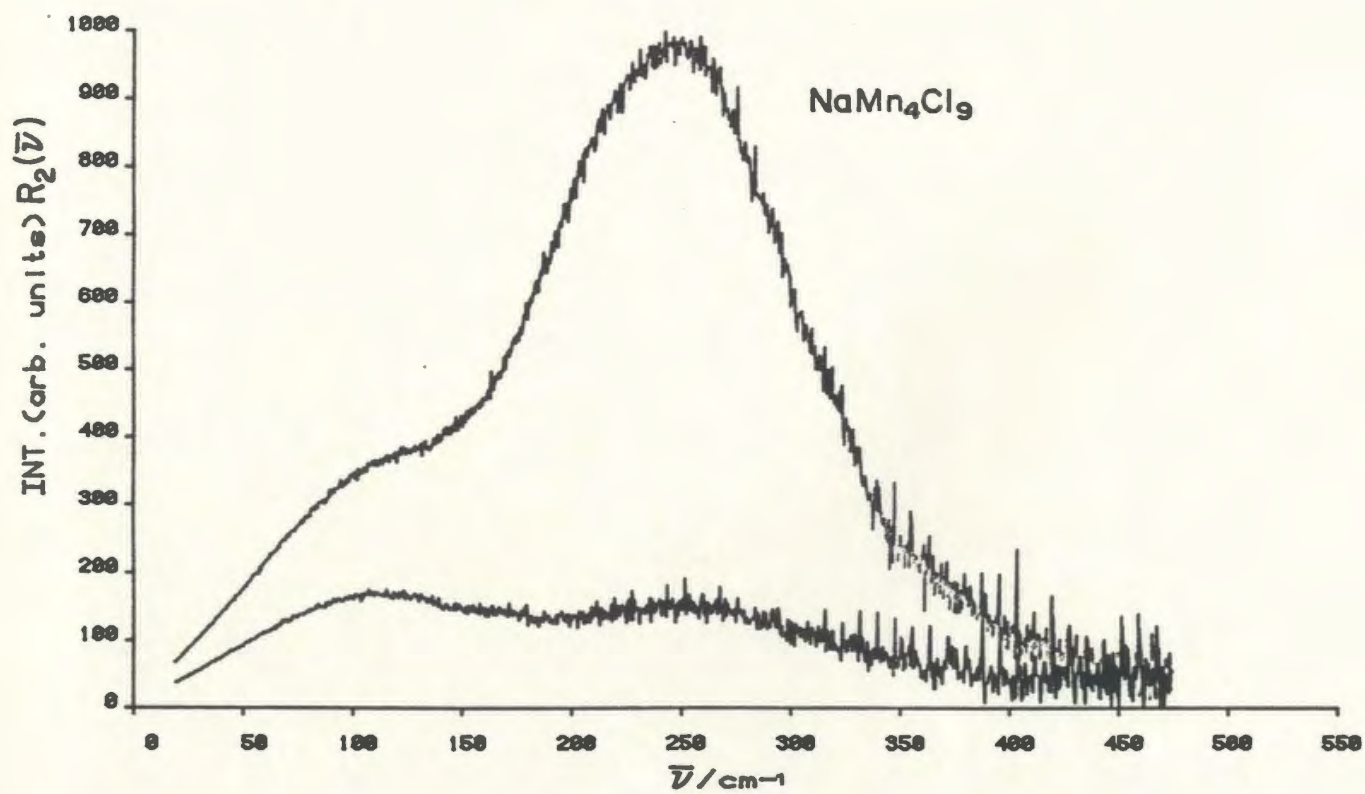
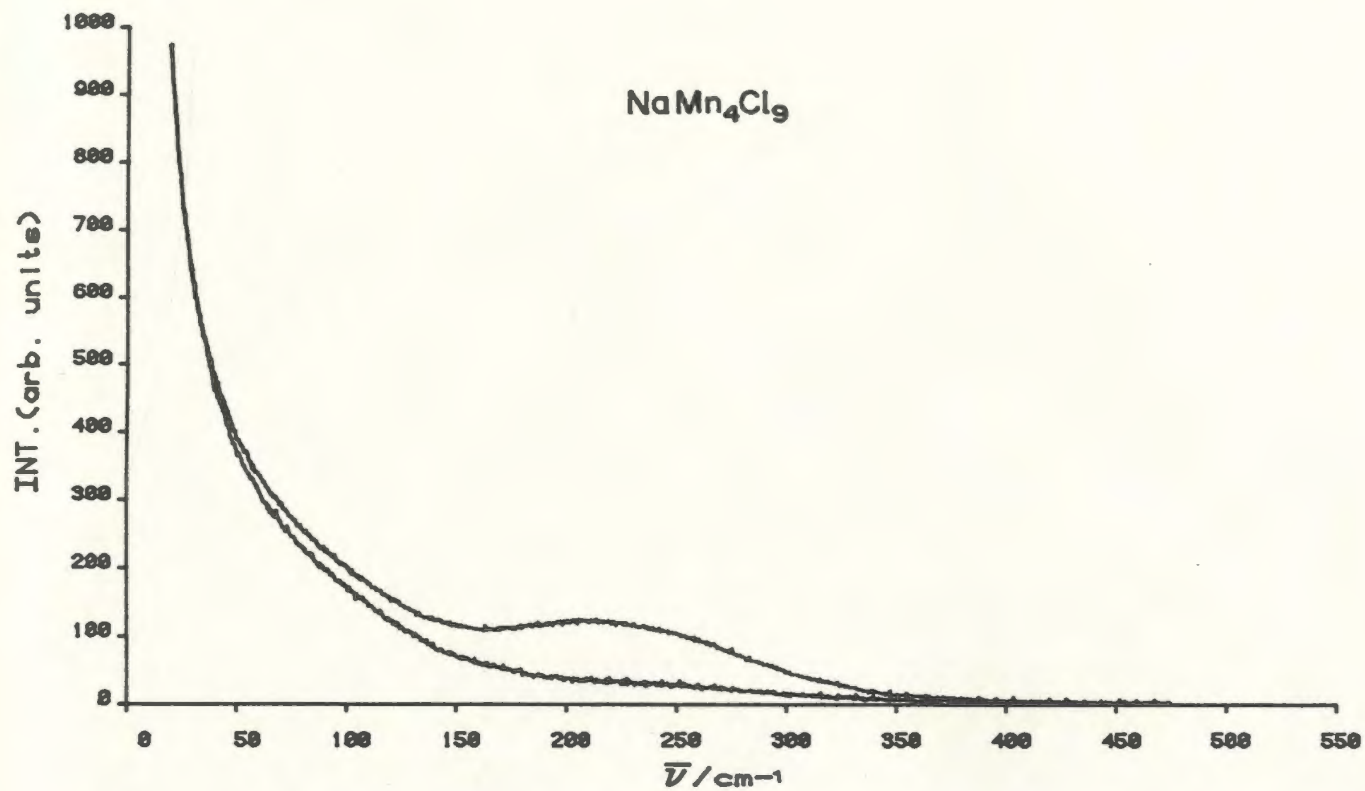




Figure 47. Raman spectra of molten  $\text{Na}_6\text{MnCl}_8$  at 988 K,  $I_{||}$   
and  $I_{\perp}$ .

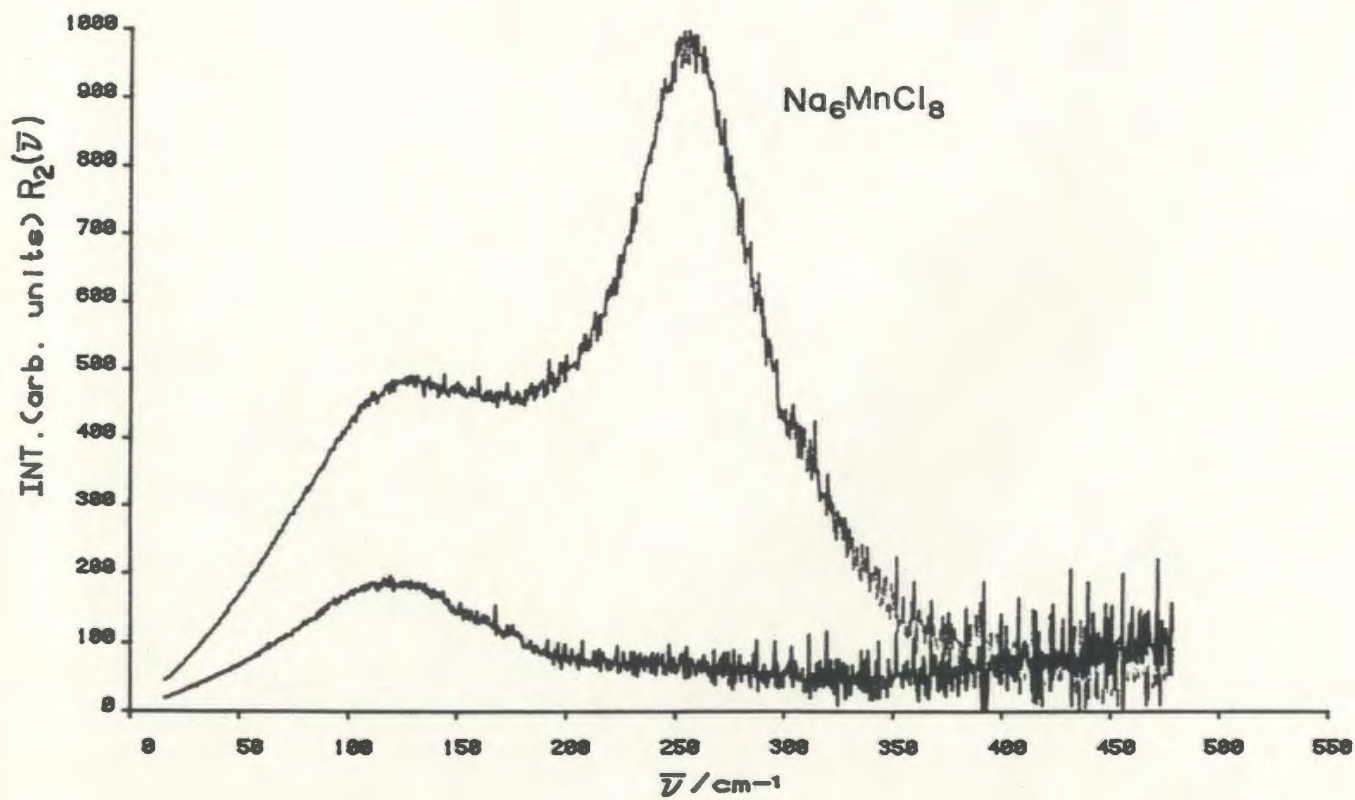
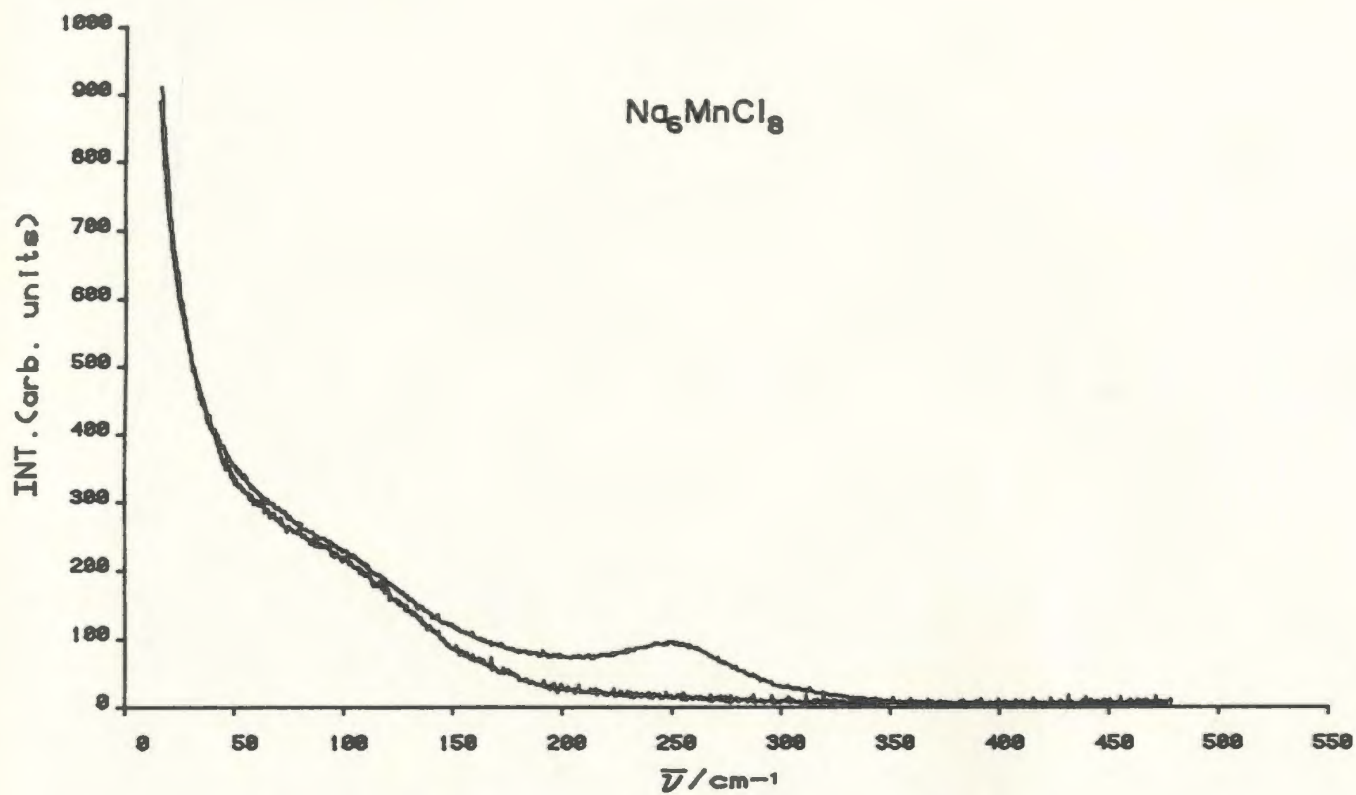


Figure 48. Isotropic Raman spectra of molten  $\text{NaMnCl}_3$ . The smooth line is the best-fit curve calculated as a sum of two Gaussian\*Lorentzian functions. The second low frequency peak has only been added to improve the base line.



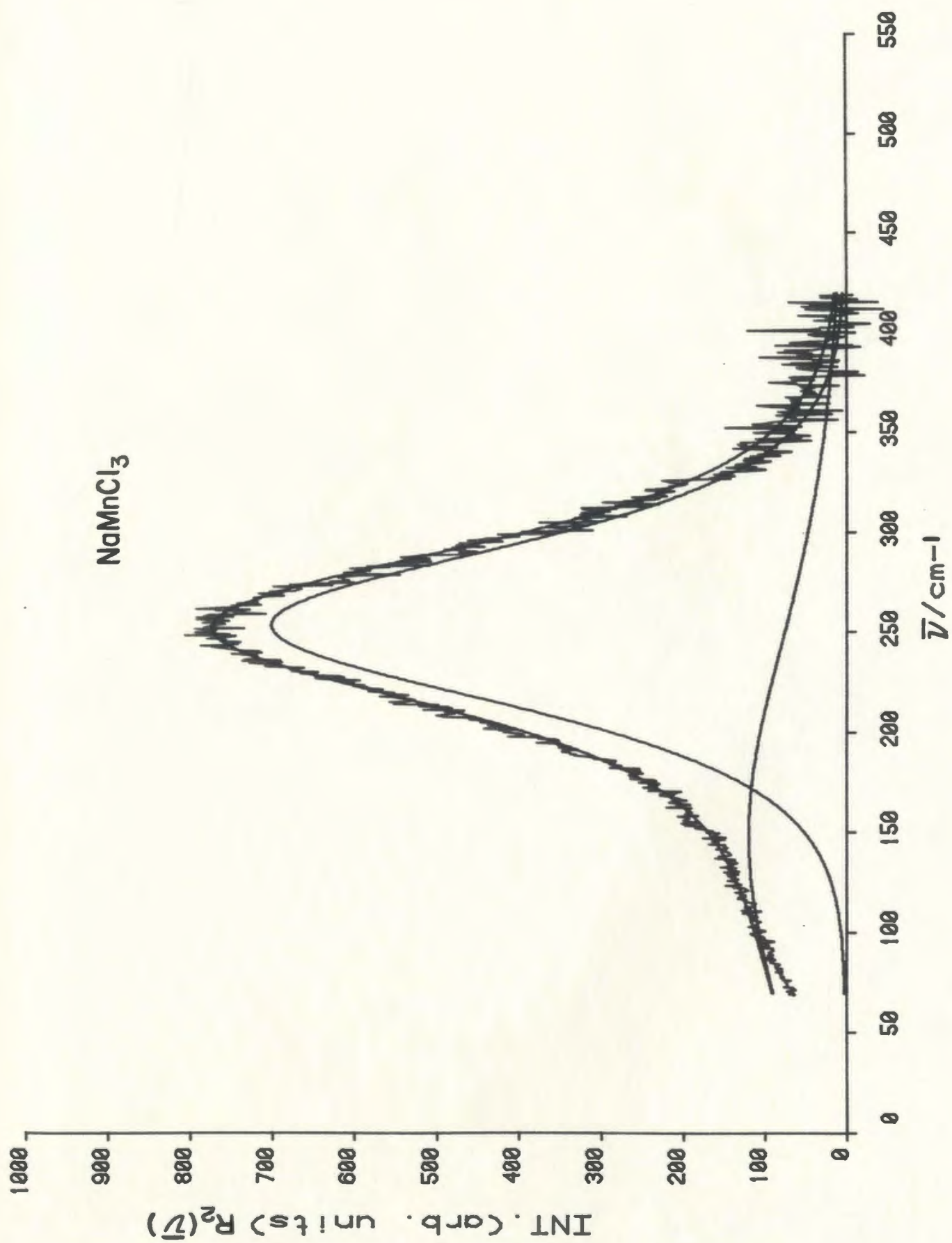


Figure 49. Isotropic Raman spectra of molten  $\text{Na}_2\text{MnCl}_4$ . The smooth line is the best-fit curve calculated as a sum of two Gaussian\*Lorentzian functions. The second low frequency peak has only been added to improve the base line.

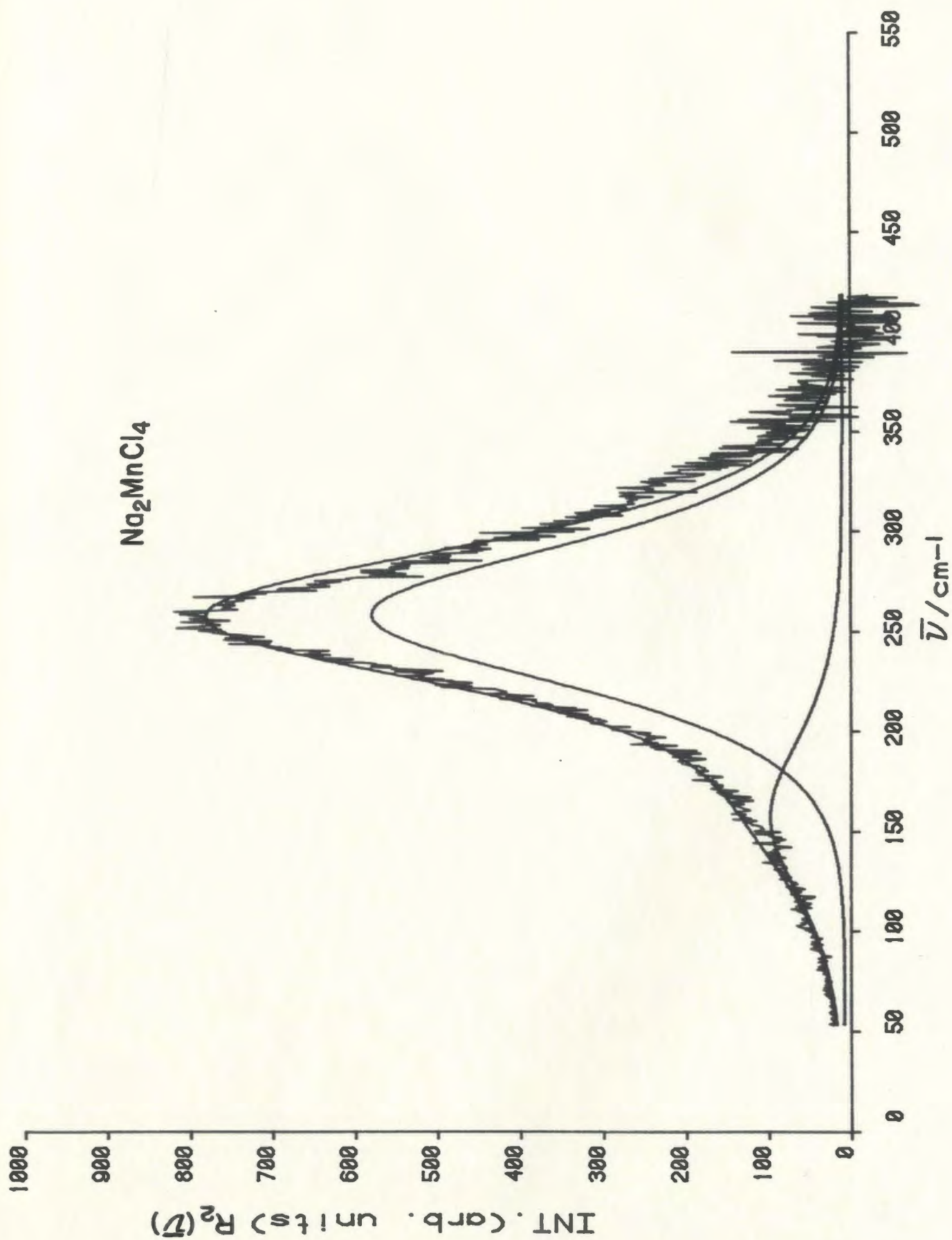




Figure 50. Isotropic Raman spectra of molten  $\text{NaCl}:\text{MnCl}_2$  (3:1).  
The smooth line is the best-fit curve calculated as a sum of two Gaussian\*Lorentzian functions. The second low frequency peak has only been added to improve the base line.

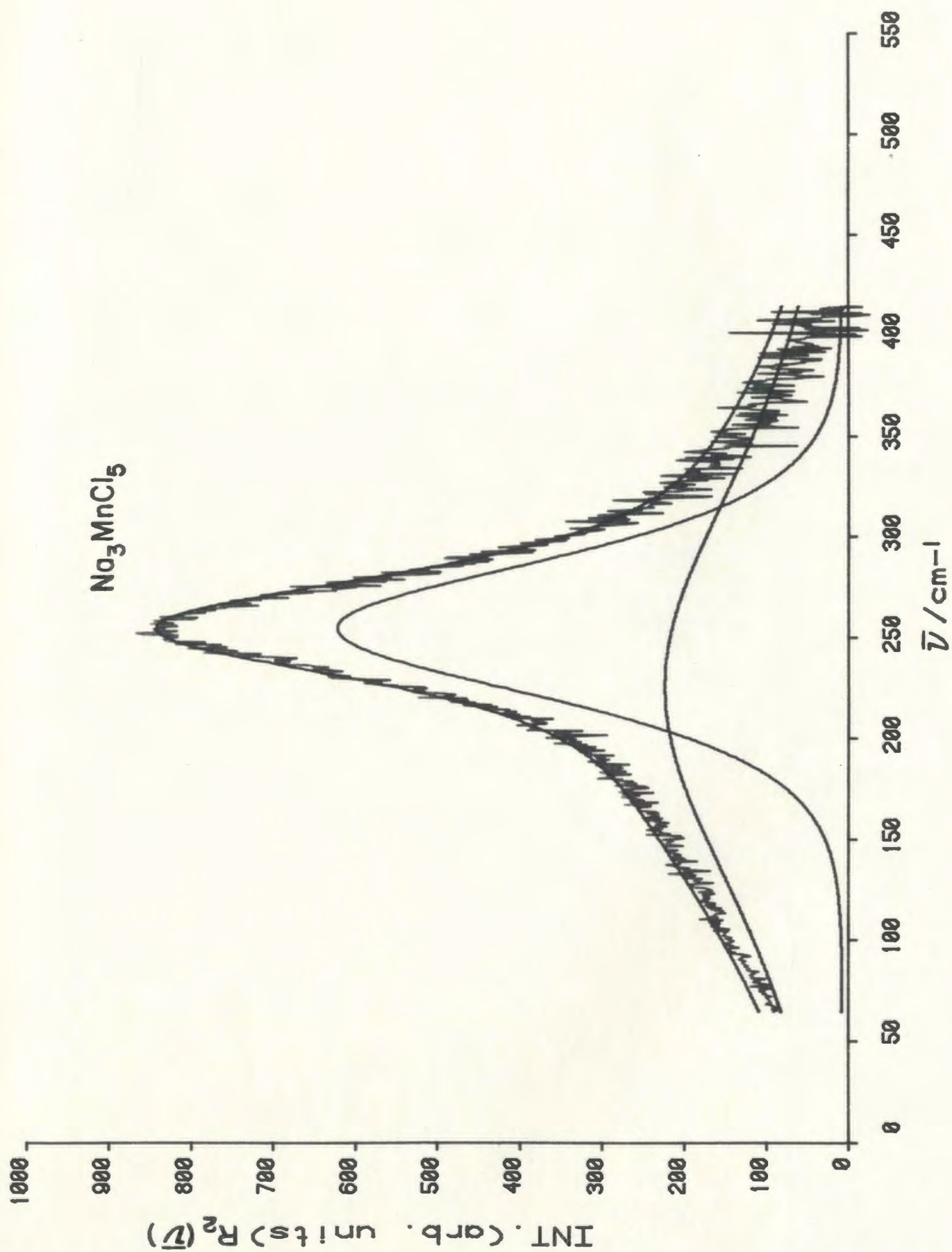


Figure 51. Isotropic Raman spectra of molten  $\text{Na}_2\text{Mn}_3\text{Cl}_8$ . The smooth line is the best-fit curve calculated with a single Gaussian\*Lorentzian function.





Figure 52. Isotropic Raman spectra of molten  $\text{NaMn}_4\text{Cl}_9$ . The smooth line is the best-fit curve calculated with a single Gaussian\*Lorentzian function.

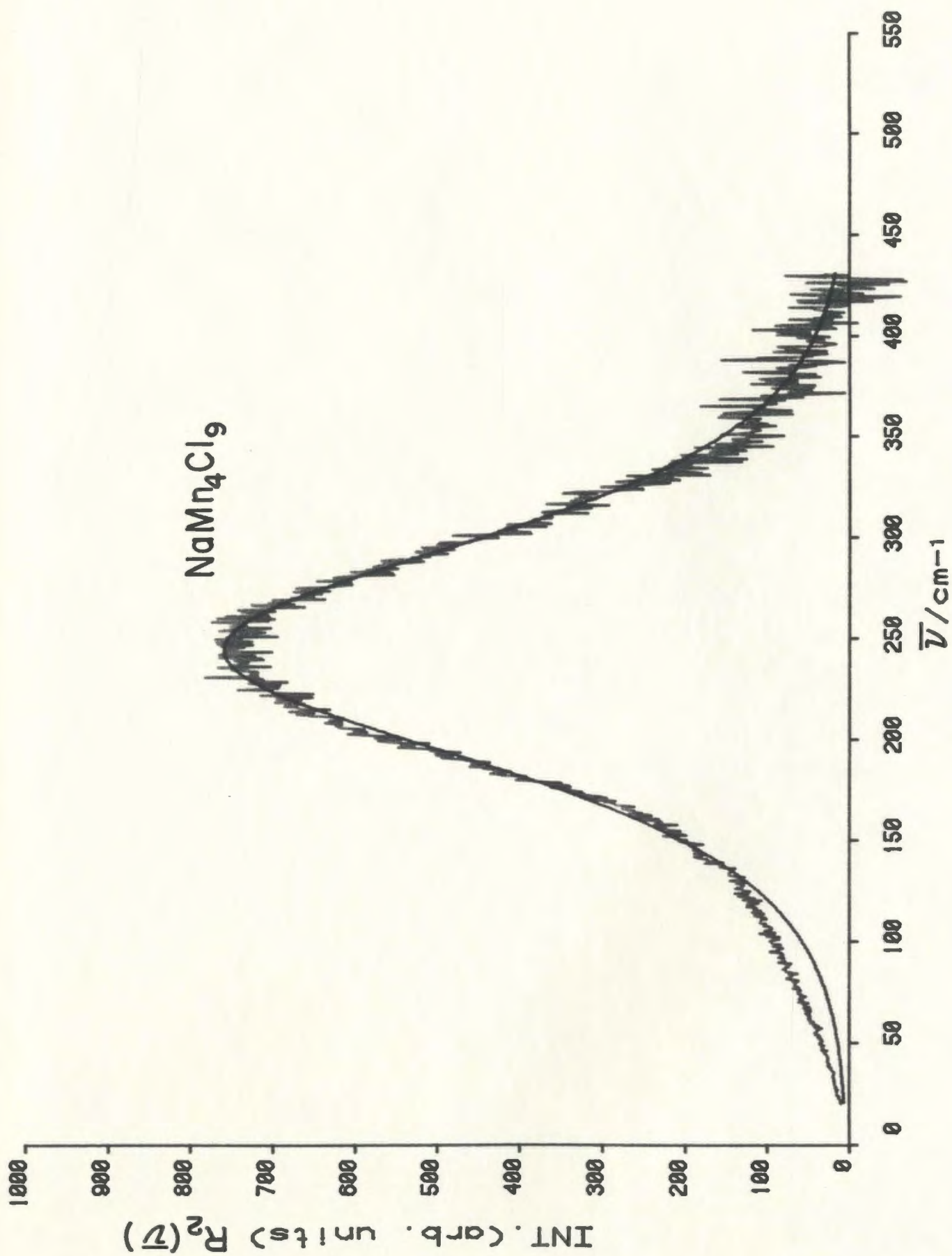
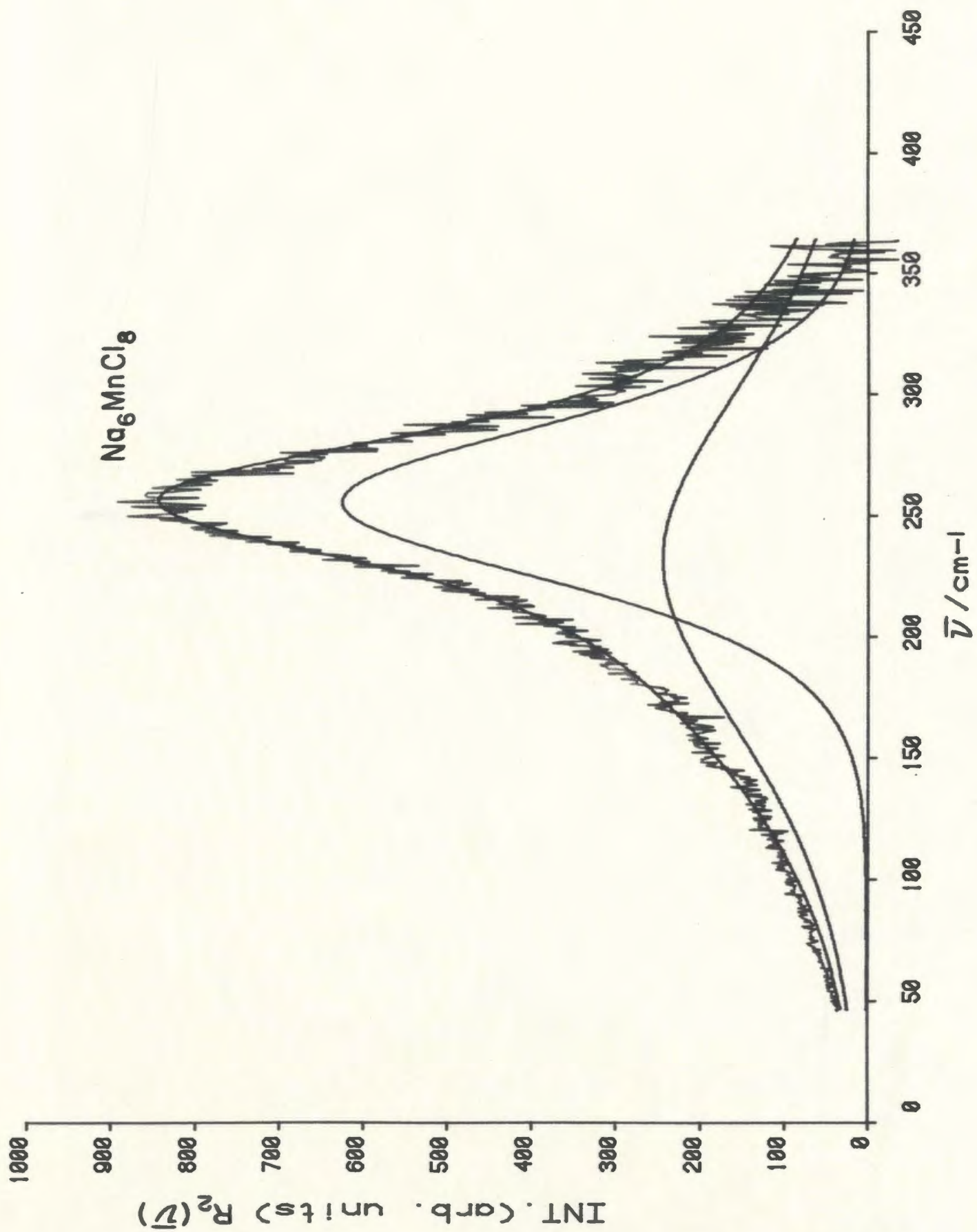




Figure 53. Isotropic Raman spectra of molten  $\text{Na}_6\text{MnCl}_8$ . The smooth line is the best-fit curve calculated as a sum of two Gaussian\*Lorentzian functions. The second low frequency peak has only been added to improve the base line.



The polarized peak from the  $R_2(\bar{\nu})$  spectrum was fitted to Gaussian\*Lorentzian function. The results are shown in figures 48, 49, 50, 51, 52 and 53. The half band width in  $\text{cm}^{-1}$ , the intensity, and the frequency in  $\text{cm}^{-1}$  for the symmetric mode  $\nu_1$  are shown in Table 23. For the NaCl-MnCl<sub>2</sub> mixtures only it was necessary to add a second component to account for excess scattering in the  $R_{2\alpha}(\bar{\nu})$  spectrum at low  $\bar{\nu}$ . The excess scattering could be due to the Na<sup>+</sup>Cl<sup>-</sup> pair which may contribute in this region<sup>22</sup> or it could be just poor baseline subtraction.

#### 4.2.5 MnCl<sub>2</sub>-LiCl Melts

The Raman spectra of MnCl<sub>2</sub>:LiCl (1:1), MnCl<sub>2</sub>:LiCl (1:2), MnCl<sub>2</sub>:LiCl (1:3) melts are shown in figures 54, 55 and 56. The results indicate the presence of tetrahedral MnCl<sub>4</sub><sup>2-</sup> species in the melt. The curve resolution results are shown in figures 57, 58 and 59, and tabulated in Table 24.

#### 4.2.6 Half band width of $\nu_1$ mode for AC1.MnCl<sub>2</sub> melts

The half band width of the symmetric mode ( $\nu_1$ ) increased over the cation series Cs<sup>+</sup> to Li<sup>+</sup>. This increment of the half band width is expected because<sup>17</sup> the symmetric stretching mode of the tetrahedral ion will occur in a greater range of environmental conditions in the neighborhood of the smaller and lighter Li<sup>+</sup> and Na<sup>+</sup> cations than for the larger Rb<sup>+</sup> and Cs<sup>+</sup> ions. A summary of the half band widths in  $\text{cm}^{-1}$  for (1:1), (2:1) and (3:1) AC1-MnCl<sub>2</sub> melts are collected in Table 25.



Table 24. Summary of results of curve resolution analysis for  $\text{MnCl}_2\text{-LiCl}$  Melts.

Compound	Frequency ( $\text{cm}^{-1}$ )	Intensity	Half band width ( $\text{cm}^{-1}$ )	Function
$\text{LiCl:MnCl}_2$ (3:1)	246.5	675	109.7	G * L
$\text{LiCl:MnCl}_2$ (2:1)	252.5	684	117.4	G * L
$\text{LiCl:MnCl}_2$ (1:1)	249.2	644	123.9	G * L

G: Gaussian, L: Lorentzian

Figure 54. Raman spectra of molten  $\text{LiCl:MnCl}_2$  (1:1) at 945 K,  $I_{||}$  and  $I_{\perp}$ .

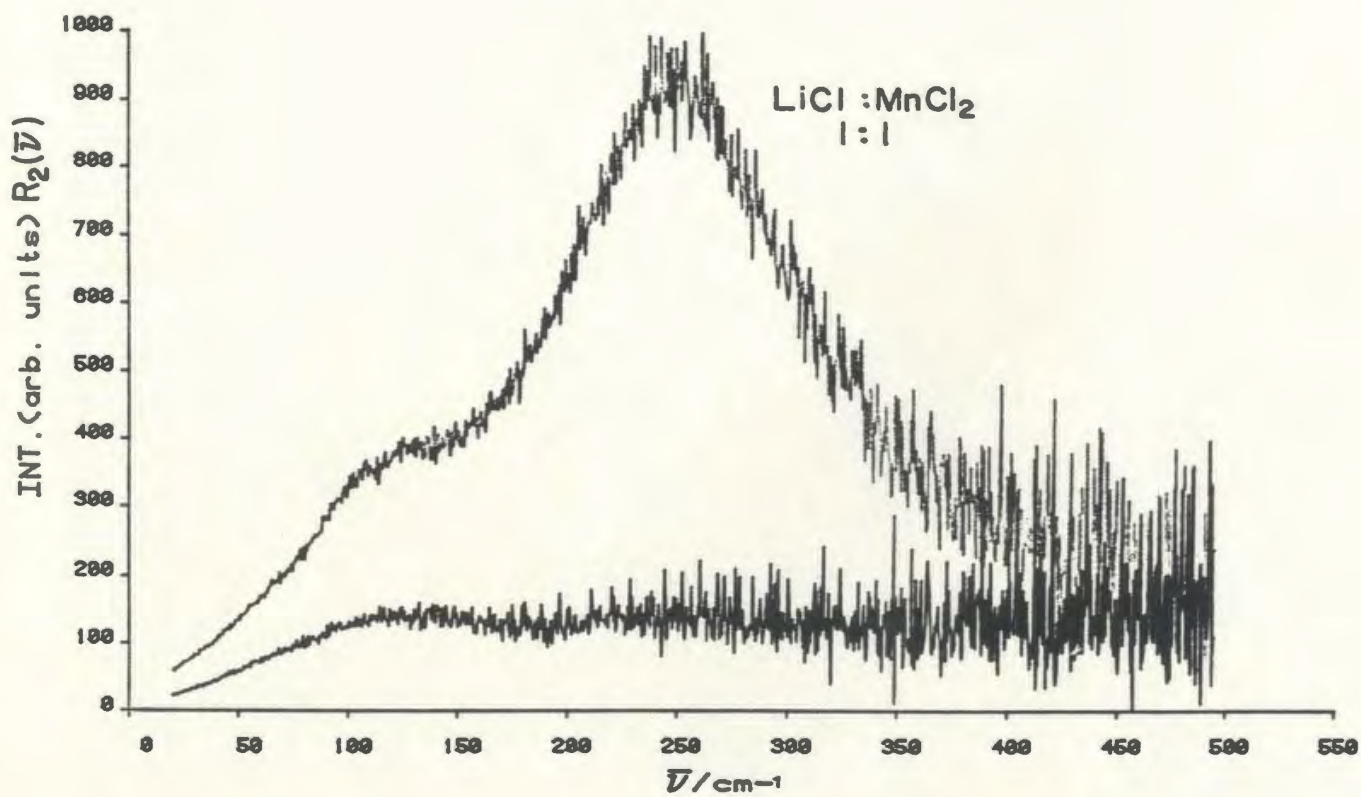
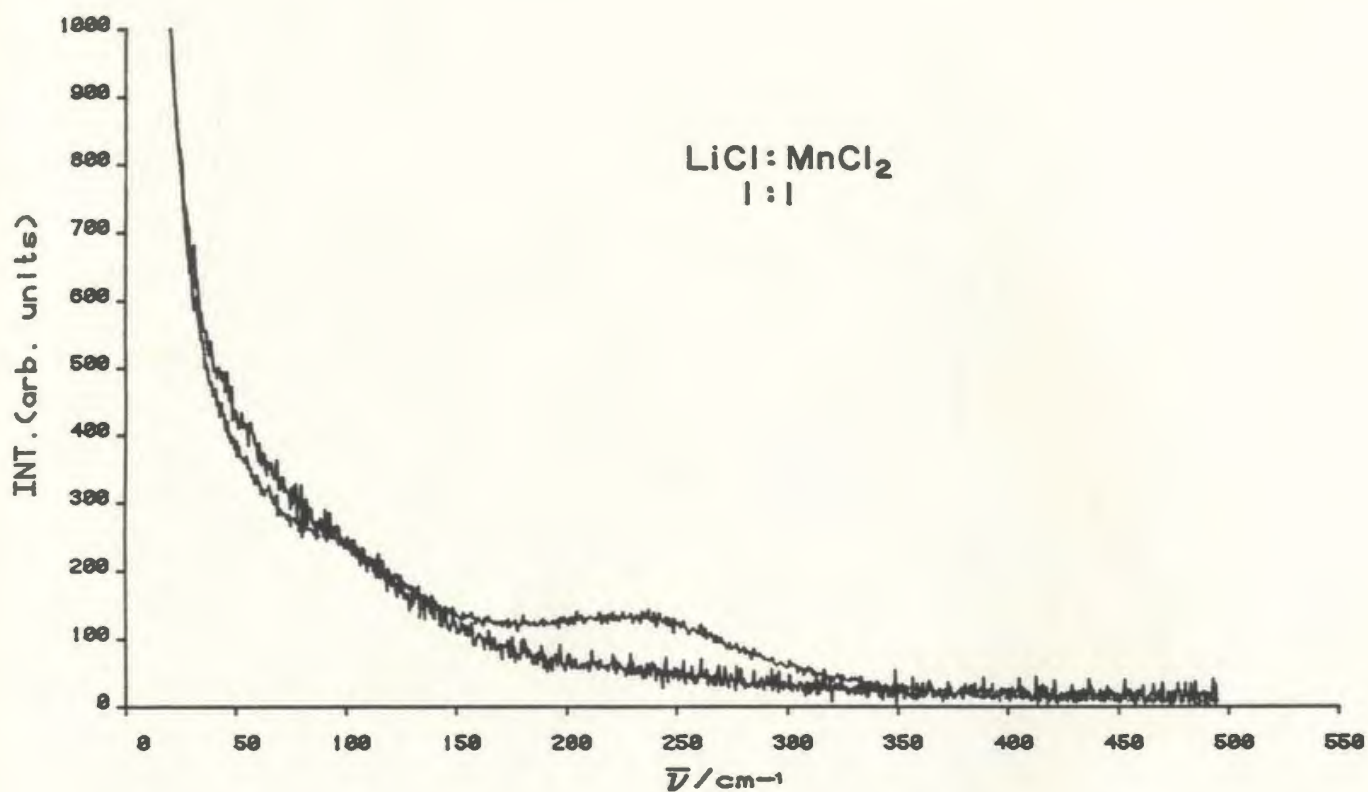




Figure 55. Raman spectra of molten  $\text{LiCl}:\text{MnCl}_2$  (2:1) at 953 K,  $I_{||}$  and  $I_{\perp}$ .

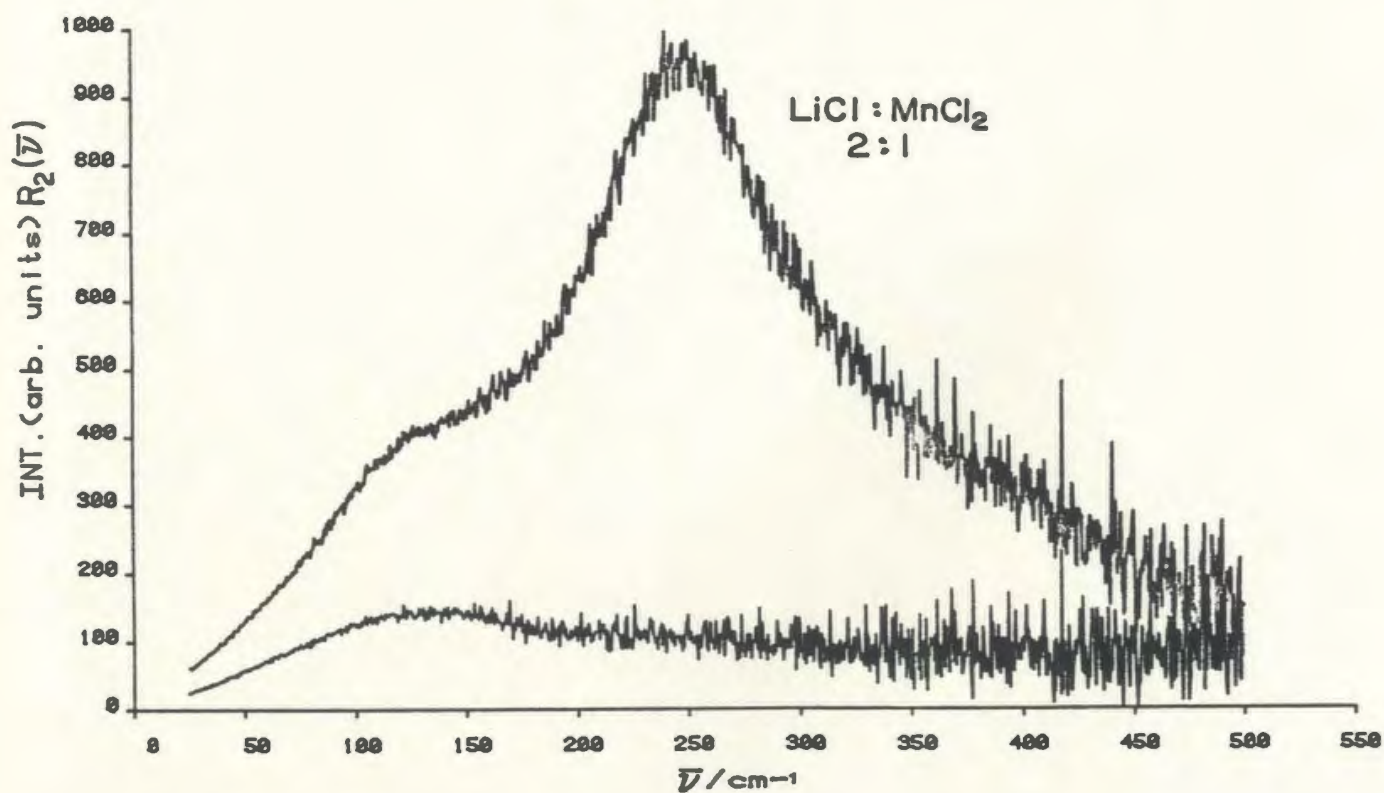
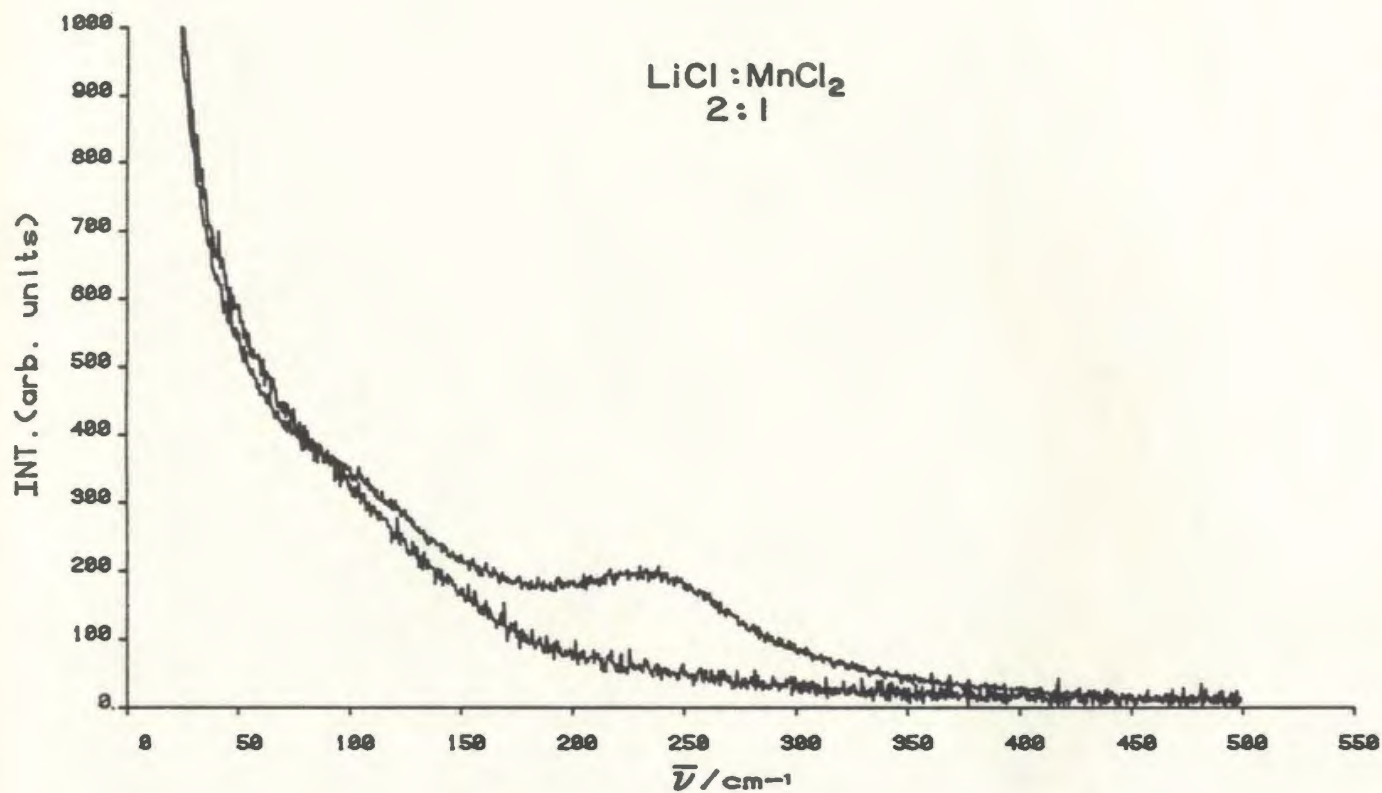


Figure 56. Raman spectra of molten  $\text{LiCl:MnCl}_2$  (3:1) at  
973 K,  $I_{||}$  and  $I_{\perp}$ .



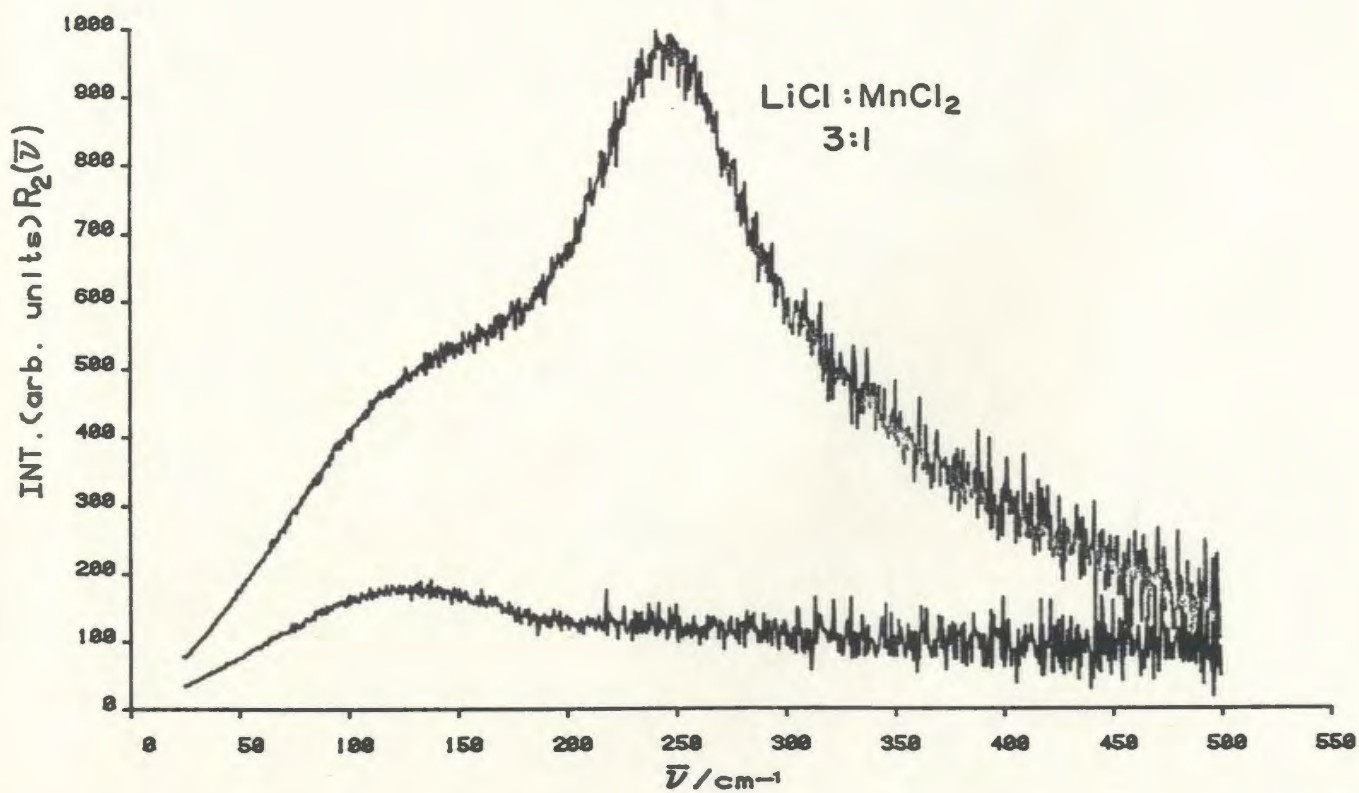
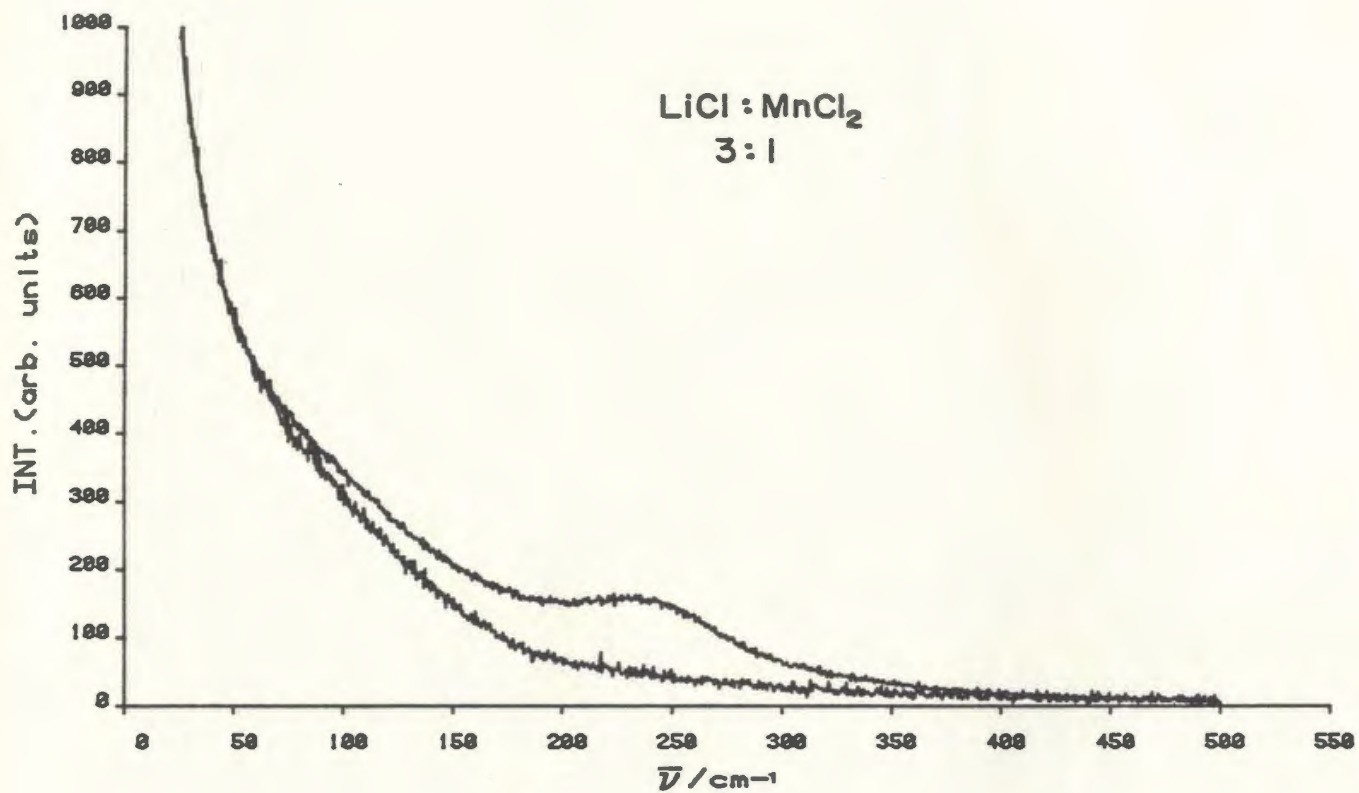


Figure 57. Isotropic Raman spectra of molten  $\text{LiCl:MnCl}_2$  (1:1).  
The smooth line is the best-fit curve calculated with  
a single Gaussian\*Lorentzian function.

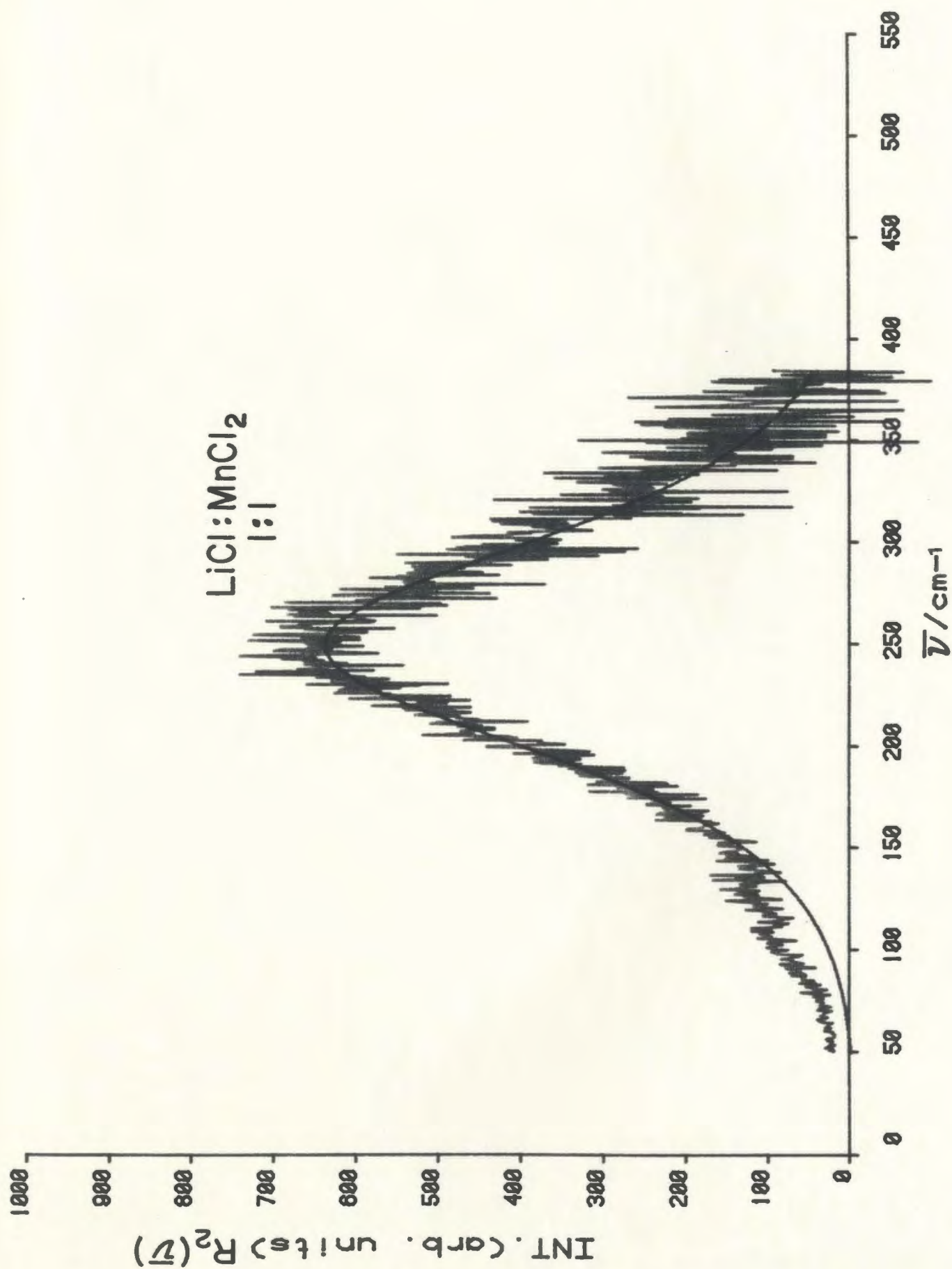




Figure 58. Isotropic Raman spectra of molten  $\text{LiCl}:\text{MnCl}_2$  (2:1).  
The smooth line is the best-fit curve calculated with  
a single Gaussian\*Lorentzian function.

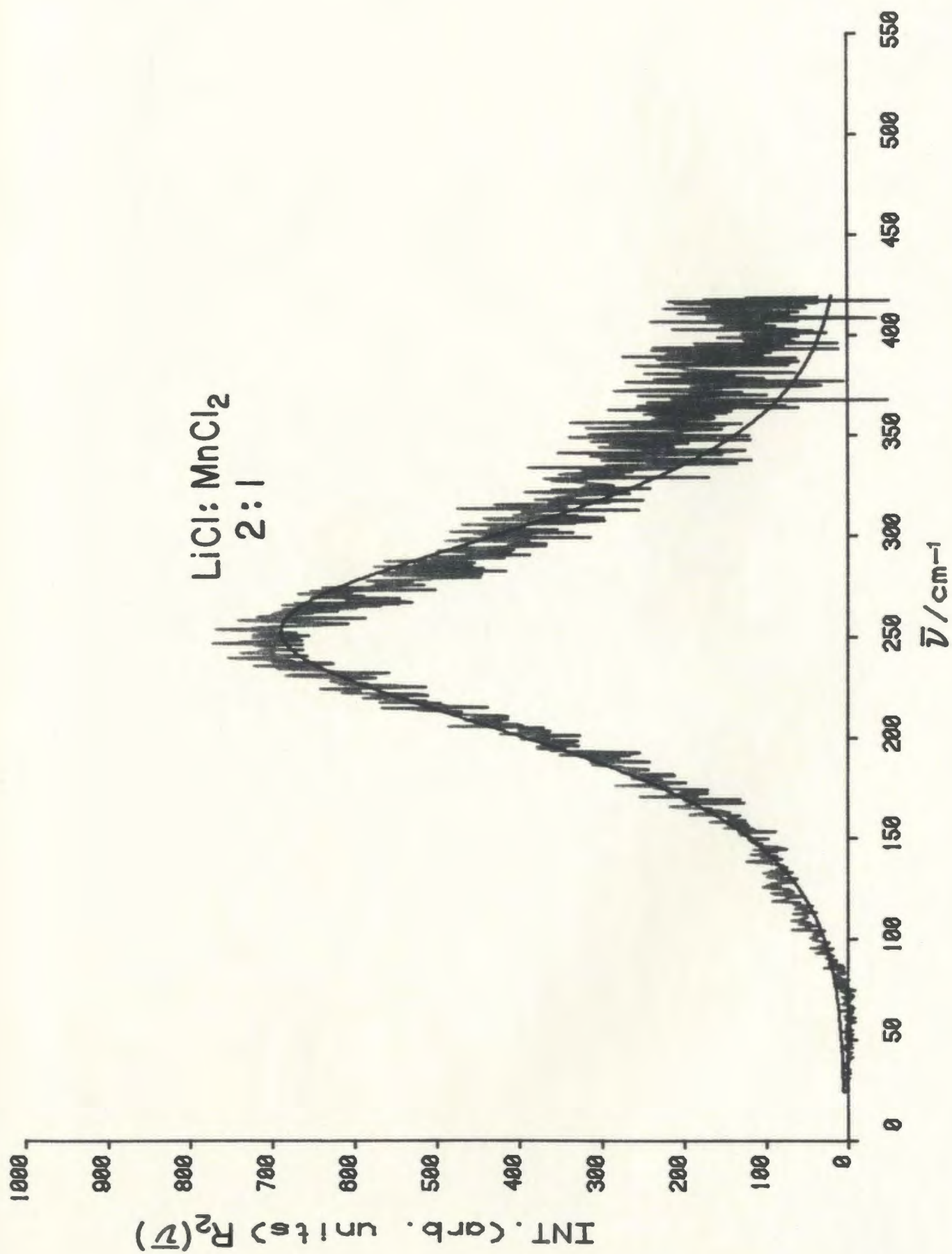


Figure 59. Isotropic Raman spectra of molten  $\text{LiCl:MnCl}_2$  (3:1).  
The smooth line is the best-fit curve calculated with  
a single Gaussian\*Lorentzian function.



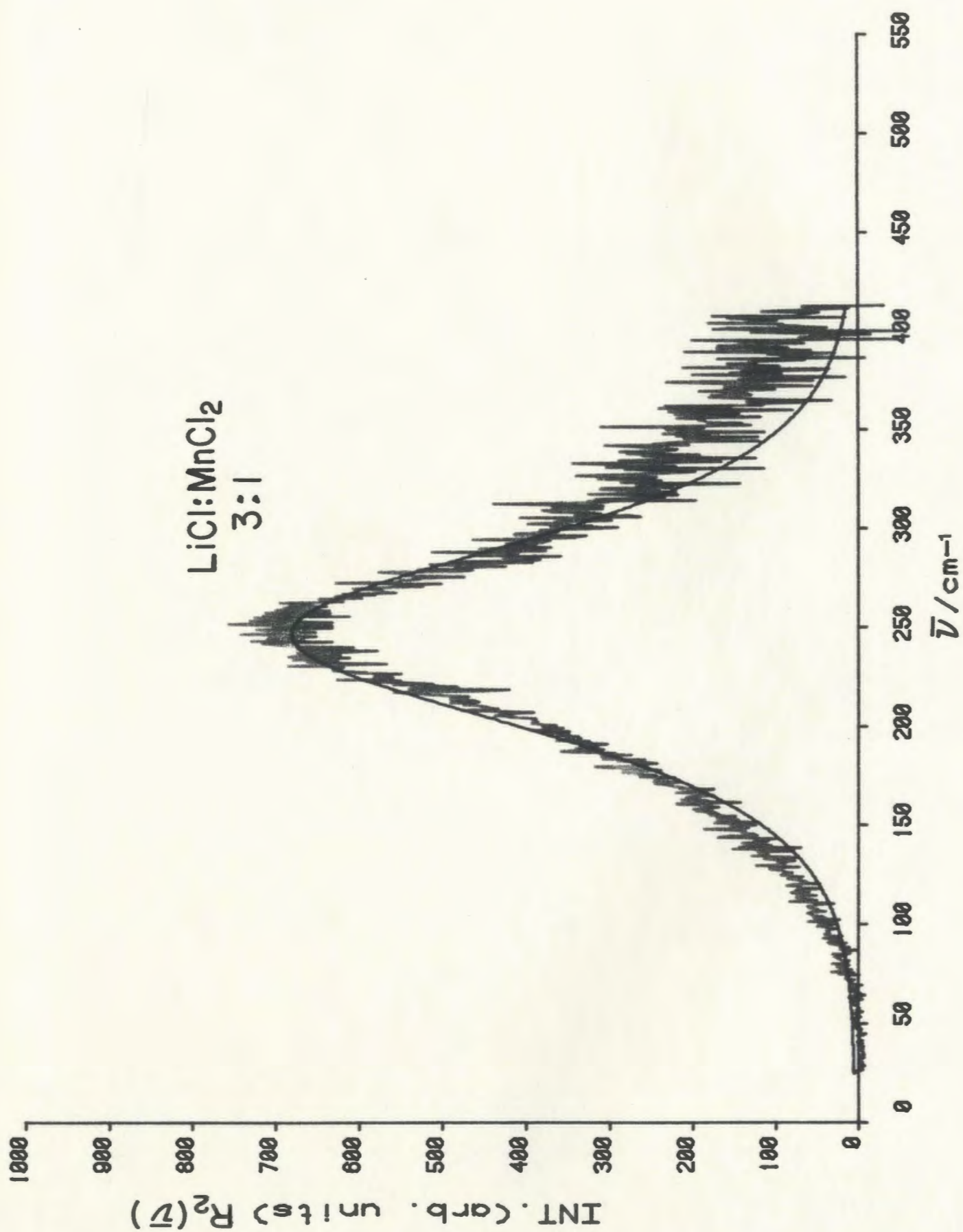


Table 25. Half band width for  $ACl-MnCl_2$  melts.

Cations	Cs	Rb	K	Na	Li
$ACl:MnCl_2$ 1:1	81.8	85.1	86.7	92.3	123.9
$ACl:MnCl_2$ 2:1	39.9	42.5	51.4	82.0	117.4
$ACl:MnCl_2$ 3:1	35.3	41.0	48.2	79.4	109.7

### 4.3 Raman Studies of $\text{MgCl}_2 \cdot n\text{ACl}$ : Molten State

#### 4.3.1 $\text{MgCl}_2$ and $\text{MgCl}_2$ -CsCl Melts

The Raman spectra of  $\text{CsCl}:\text{MgCl}_2$  (4:1),  $\text{Cs}_2\text{MgCl}_4$ ,  $\text{CsCl}:\text{MgCl}_2$  (1.5:1),  $\text{CsMgCl}_3$ ,  $\text{CsCl}:\text{MgCl}_2$  (0.5:1), and  $\text{MgCl}_2$  melts are shown in figures 60, 61, 62, 63, 64 and 65 respectively. For melts of composition  $\text{MgCl}_2 \cdot n\text{CsCl}$  for  $n \geq 2$  there is a strong, sharp polarized peak at  $250 \text{ cm}^{-1}$  which may be assigned to  $\nu_1$  mode of  $\text{MgCl}_4^{2-}$  ion. A depolarized band due to  $\nu_3$  is observed as a very weak peak in the range  $335\text{-}355 \text{ cm}^{-1}$ , and previously was observed in the infrared mull spectrum<sup>13</sup> of  $\text{MgCl}_4^{2-}$  ion as a very strong peak at  $360 \text{ cm}^{-1}$ . The depolarized peaks due to  $\nu_2$  and  $\nu_4$  are observed in the region  $100\text{-}150 \text{ cm}^{-1}$ . Since one polarized peak is clearly resolved at  $250 \text{ cm}^{-1}$ , and three depolarized peaks are observed, the results strongly indicate the formation of  $\text{MgCl}_4^{2-}$  ions in  $\text{CsCl}:\text{MgCl}_2$  (4:1) melt. In the melts of composition  $\text{MgCl}_2 \cdot n\text{CsCl}$  for  $n \leq 2$  the polarized feature consists of at least two overlapped peaks estimated at  $225$  and  $250 \text{ cm}^{-1}$  and one broad shoulder around  $\sim 300 \text{ cm}^{-1}$ . The intensity of the low frequency peak  $\sim 225 \text{ cm}^{-1}$  and the high frequency peak at  $300 \text{ cm}^{-1}$  quite clearly increase in relative intensity with increasing  $\text{MgCl}_2$  concentration, figures 61, 62 and 63. The formation of a new equilibrium species in the melts of high  $\text{MgCl}_2$  concentration was suggested<sup>17</sup> based on the presence of the low frequency peak. The results indicate the existence of tetrahedral  $\text{MgCl}_4^{2-}$  species in equilibrium with another species. This new species was attributed to the  $\text{Mg}_2\text{Cl}_7^{3-}$  ion since for this structure the magnesium may retain its tetrahedral coordination through corner sharing with another tetrahedral ion. A  $\text{Mg}_2\text{Cl}_6^{2-}$  ion in which the magnesium is tetrahedrally coordinated through edge sharing with another tetrahedral ion would also be logical.



These results are exactly parallel to the case of  $\text{AlCl}_3 \cdot \text{AlCl}$  melts<sup>2</sup> where two well resolved peaks at  $\sim 310$  and  $430 \text{ cm}^{-1}$  due to the symmetric stretching motions of the  $\text{Al}_2\text{Cl}_7^-$  ion increase at the expense of a peak at  $\sim 350 \text{ cm}^{-1}$  due to  $\text{AlCl}_4^-$  for melts of appropriate molar ratio. The greater band overlap in the  $\text{MgCl}_2 \cdot \text{AlCl}$  system is caused by environmental broadening factors such as the weaker bond energy and thermal motion.

The results of curve resolution analysis of the  $I_\alpha(\bar{\nu})$  spectra are shown in figures 66 to 71 and Table 26. Excellent fits for the  $\text{MgCl}_2 \cdot n\text{CsCl}$  melts with  $n = 2.0, 1.5$  and  $1.0$  were achieved with the three band model for peaks at  $\sim 220, 250$  and  $300 \text{ cm}^{-1}$ . Two band fits gave poor agreement with the observed spectra and were physically unrealistic. The intensity ratio of the peaks at 220 and 300 increased together at the expense of intensity at  $250 \text{ cm}^{-1}$  as the  $\text{MgCl}_2$  concentration was increased (ie. an increase of  $\text{Mg}_2\text{Cl}_7^{3-}$  versus  $\text{MgCl}_4^{2-}$ ). For melts of high  $\text{MgCl}_2$  content and pure  $\text{MgCl}_2$  the simple two species equilibrium model did not give good fits to the data because of a significant polarized intensity increase about  $150 \text{ cm}^{-1}$ . In the  $\text{AlCl}_3 \cdot \text{AlCl}$  system peaks due to  $\text{Al}_3\text{Cl}_{10}^-$  and  $\text{Al}_2\text{Cl}_6$  have been identified<sup>2</sup> but the band overlap in the  $\text{MgCl}_2 \cdot n\text{AlCl}$  systems precludes detailed analysis of melts with  $n \geq 0.5$  and the curve analysis for these systems may not be unique. A broad three band fit adequately reproduced the spectrum of pure  $\text{MgCl}_2$  melt.

Three polarized peaks may be resolved for the pure  $\text{MgCl}_2$  melt, the one resolved at  $237 \text{ cm}^{-1}$  is attributed to the symmetric stretching mode ( $\nu_1$ ) of the tetrahedral ion, while the other two polarized peaks are resolved at 194 and  $161 \text{ cm}^{-1}$  were reported previously<sup>15</sup> at 194 and  $130 \text{ cm}^{-1}$  and attributed to symmetric stretching vibrations of poly-

nuclear species  $\text{Mg}_2\text{Cl}_2^{2+}$ , or  $\text{Mg}_2\text{Cl}_3^+$ , or  $\text{Mg}_2\text{Cl}_4$ . The polarized peak resolved at  $145\text{ cm}^{-1}$  in the spectrum of  $\text{CsCl}:\text{MgCl}_2$  (0.5:1) melt appears to correspond to the one resolved at  $161\text{ cm}^{-1}$  in the spectrum of  $\text{MgCl}_2$  melt and attributed to polynuclear species. The Raman results suggest that  $\text{CsCl}:\text{MgCl}_2$  (0.5:1) melt contains an equilibrium mixture of  $\text{MgCl}_4^{2-}$  ions,  $\text{Mg}_2\text{Cl}_7^{3-}$  ions, and polynuclear species as positive or neutral ions. The presence of the depolarized peak at  $\sim 350\text{ cm}^{-1}$  in pure  $\text{MgCl}_2$  melts suggests that an  $\text{MgCl}_4^{2-}$  unit may be present. It should be emphasized that the minimum number of bands necessary to obtain a good fit was the guiding factor in the curve analysis. More bands would give better fits and could give more realistic representation species concentrations. The important consequence of the curve analysis is the fact that at least two species and probably a third must be present to generate the observed spectra. This should be contrasted to the results for the manganese chloride system discussed previously where possible species had lifetimes that were too short to give discrete peaks.

#### 4.3.2 $\text{MgCl}_2$ -KCl Melts

The Raman spectra of  $\text{K}_2\text{MgCl}_4$ ,  $\text{KCl}:\text{MgCl}_2$  (1.5:1),  $\text{KMgCl}_3$ , and  $\text{KCl}:\text{MgCl}_2$  (0.5:1) melts are shown in figures 72, 73, 74 and 75. The peaks due to  $\nu_2$  and  $\nu_4$  of the tetrahedral  $\text{MgCl}_4^{2-}$  ion are observed in the region  $100\text{--}150\text{ cm}^{-1}$ , while the peak due to  $\nu_3$  is observed as a weak peak at  $\sim 350\text{ cm}^{-1}$ . Only one broad polarized envelop is observed in each melt, and this envelop changes shape and broadens with increasing  $\text{MgCl}_2$  concentration. The broadening of the polarized feature indicates that there is another species in equilibrium with the tetrahedral  $\text{MgCl}_4^{2-}$  ions. The curve analysis gives results similar to the  $\text{CsCl}$



Table 26. Summary of results of curve resolution analysis for  $\text{MgCl}_2$  and  $\text{MgCl}_2$ -CsCl Melts.

Compound	Frequency ( $\text{cm}^{-1}$ )	Intensity	Half band width ( $\text{cm}^{-1}$ )	Assignments
$\text{CsCl}:\text{MgCl}_2$ (4:1)	249.6	334	23.0	$(\nu_1) \text{MgCl}_4^{2-}$
$\text{Cs}_2\text{MgCl}_4$	225.4	99	44.7	$(\nu) \text{Mg}_2\text{Cl}_7^{3-}$
	250.1	361	24.6	$(\nu_1) \text{MgCl}_4^{2-}$
	297.0	25	56.7	$(\nu) \text{Mg}_2\text{Cl}_7^{3-}$
$\text{CsCl}:\text{MgCl}_2$ (1.5:1)	224.6	138	55.4	$(\nu) \text{Mg}_2\text{Cl}_7^{3-}$
	250.0	189	27.1	$(\nu_1) \text{MgCl}_4^{2-}$
	294.8	28	72.9	$(\nu) \text{Mg}_2\text{Cl}_7^{3-}$
$\text{CsMgCl}_3$	220.6	200	57.4	$(\nu) \text{Mg}_2\text{Cl}_7^{3-}$
	250.6	160	35.9	$(\nu_1) \text{MgCl}_4^{2-}$
	291.8	42	103.2	$(\nu) \text{Mg}_2\text{Cl}_7^{3-}$
$\text{CsCl}:\text{MgCl}_2$ (0.5:1)	145.4	47	66.1	$(\nu)$ polynuclear species
	213.3	155	55.8	$(\nu) \text{Mg}_2\text{Cl}_7^{3-}$
	244.5	146	63.0	$(\nu_1) \text{MgCl}_4^{2-}$
	315.7	12	112.3	$(\nu) \text{Mg}_2\text{Cl}_7^{3-}$
$\text{MgCl}_2$	161.1	248	204.3	$(\nu)$ polynuclear species
	194.2	163	52.9	
	237.0	129	71.4	$(\nu_1) \text{MgCl}_4^{2-}$



Figure 60. Raman spectra of molten  $\text{CsCl:MgCl}_2$  (4:1) at  
840 K,  $I_{||}$  and  $I_{\perp}$ .

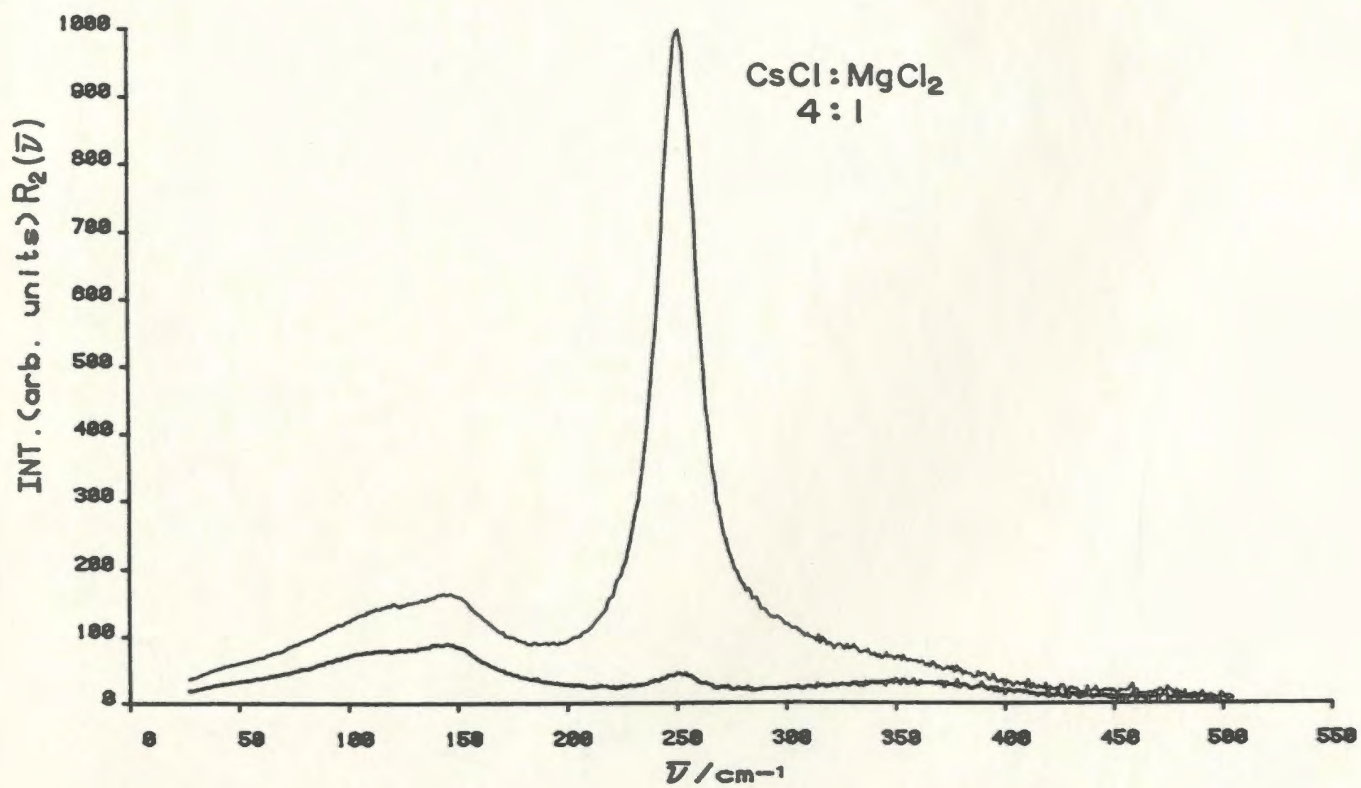
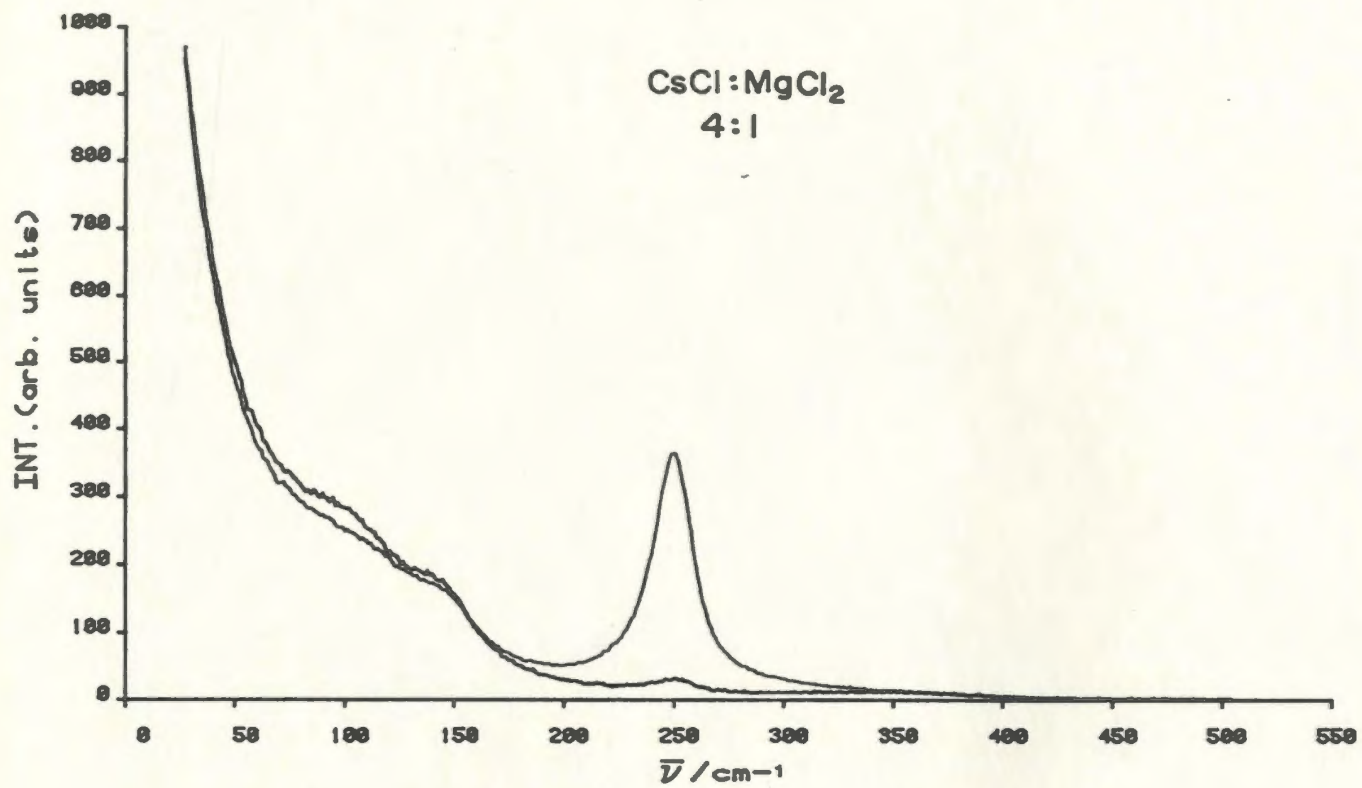


Figure 61. Raman spectra of molten  $\text{Cs}_2\text{MgCl}_4$  at 896 K,

$I_{||}$  and  $I_{\perp}$ .



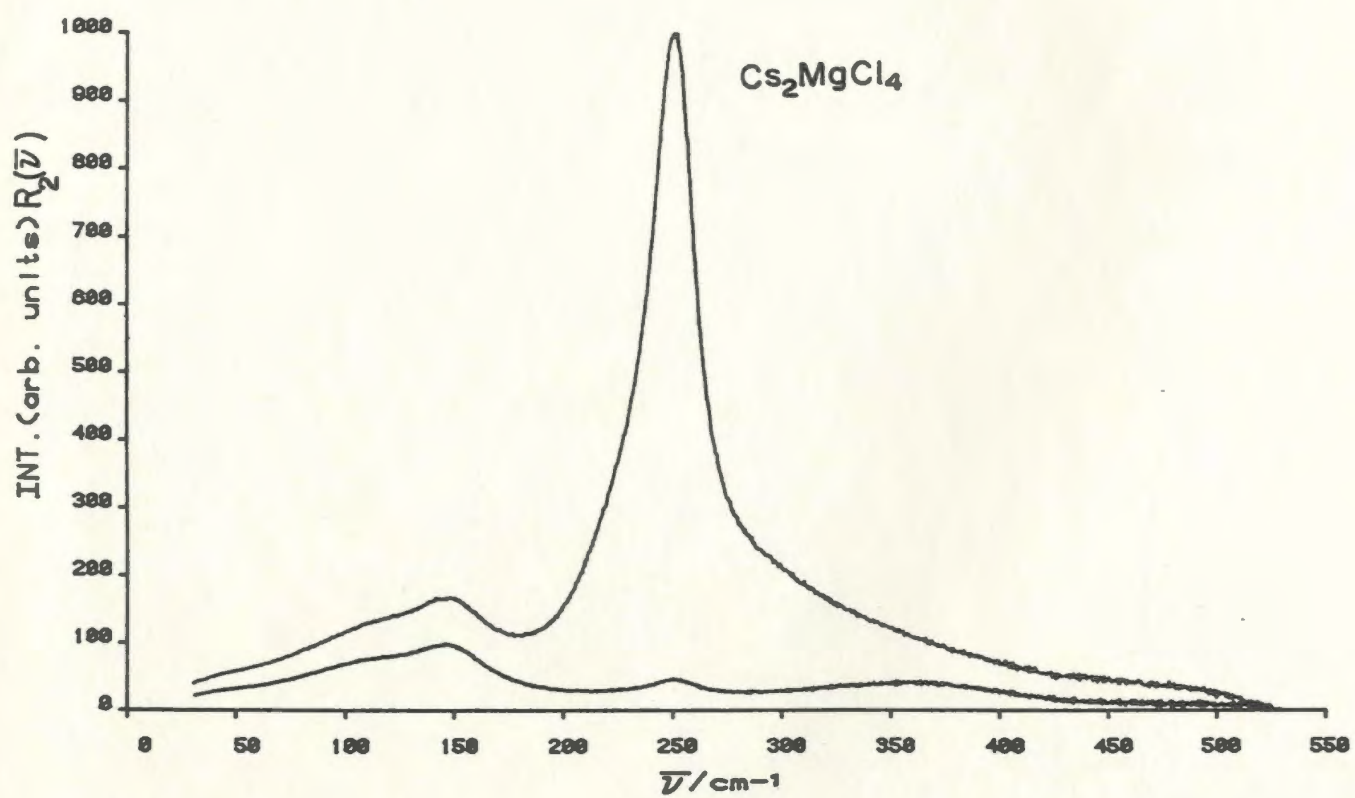
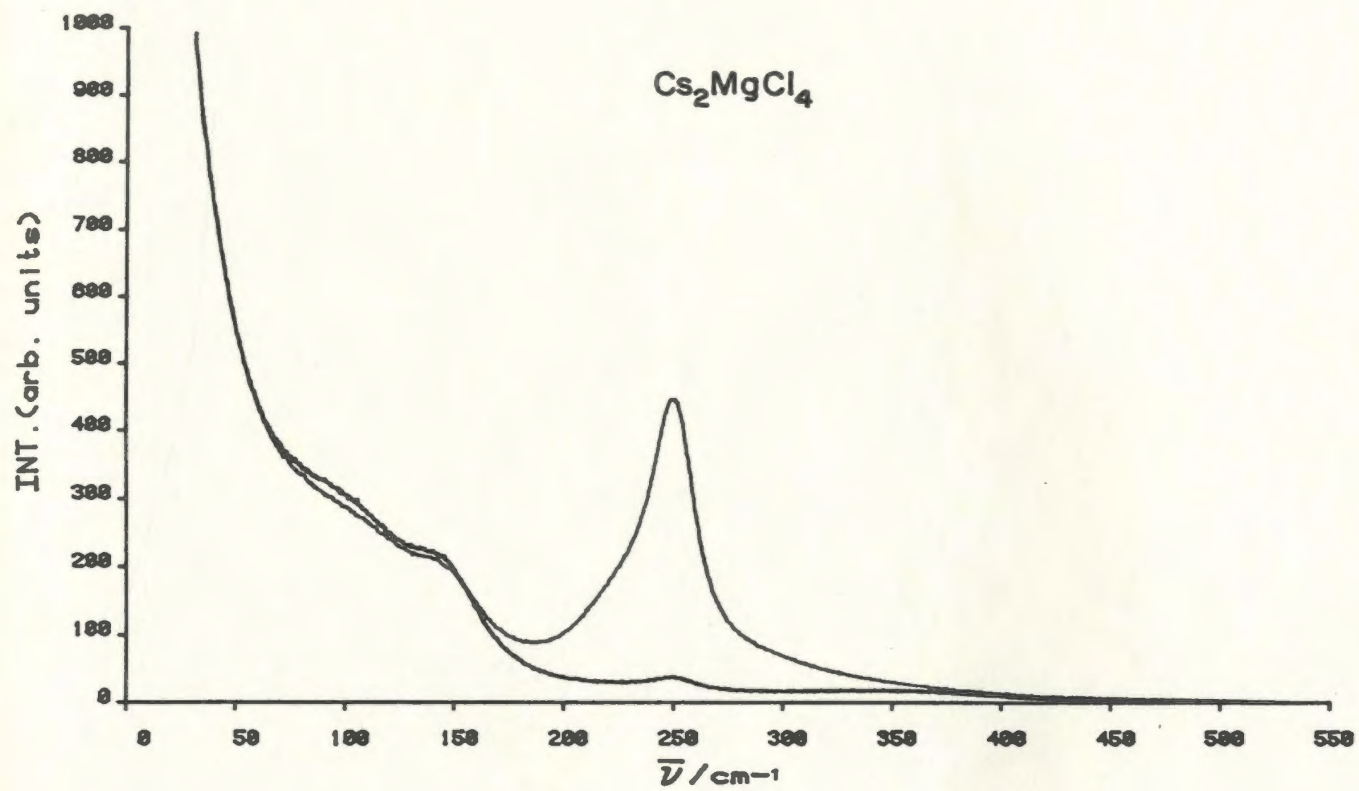


Figure 62. Raman spectra of molten  $\text{CsCl:MgCl}_2$  (1.5:1) at  
915 K,  $I_{||}$  and  $I_{\perp}$ .

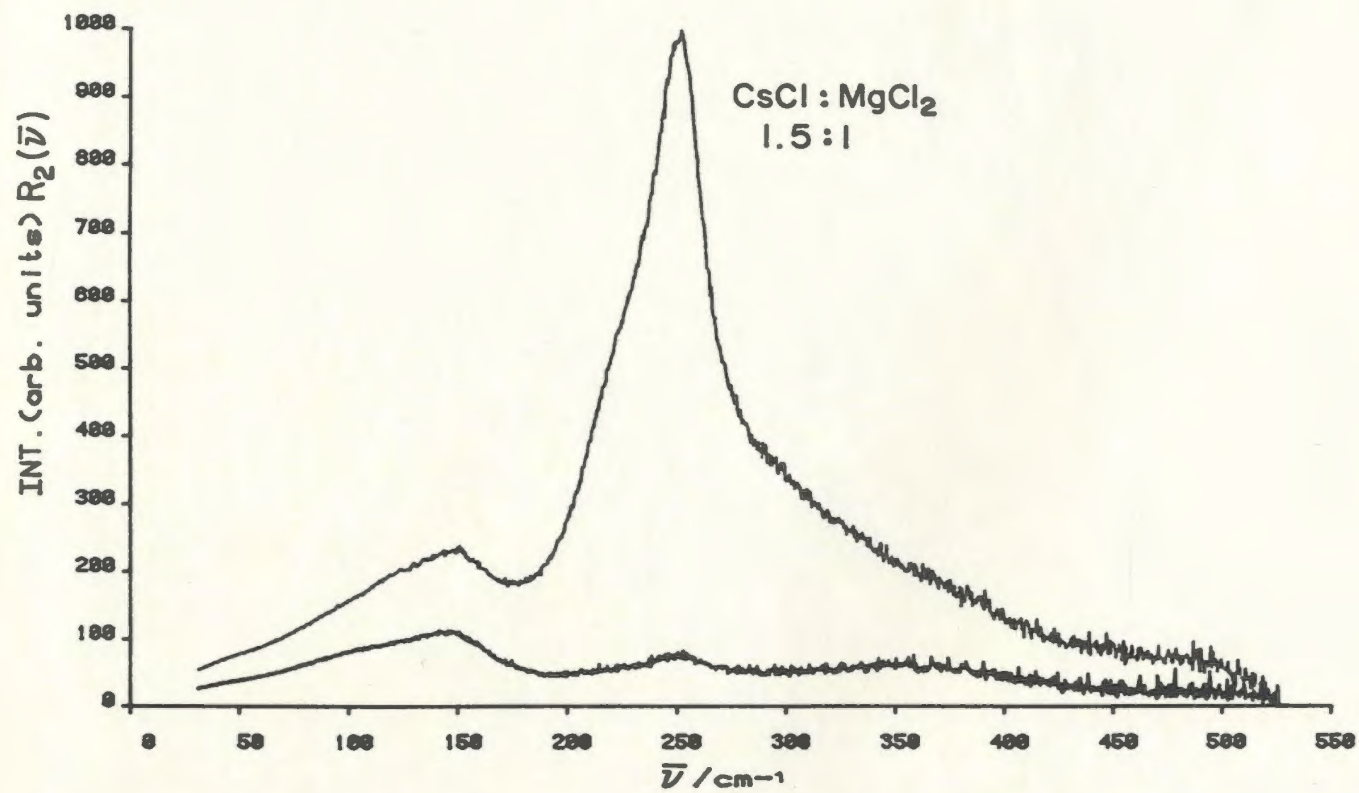
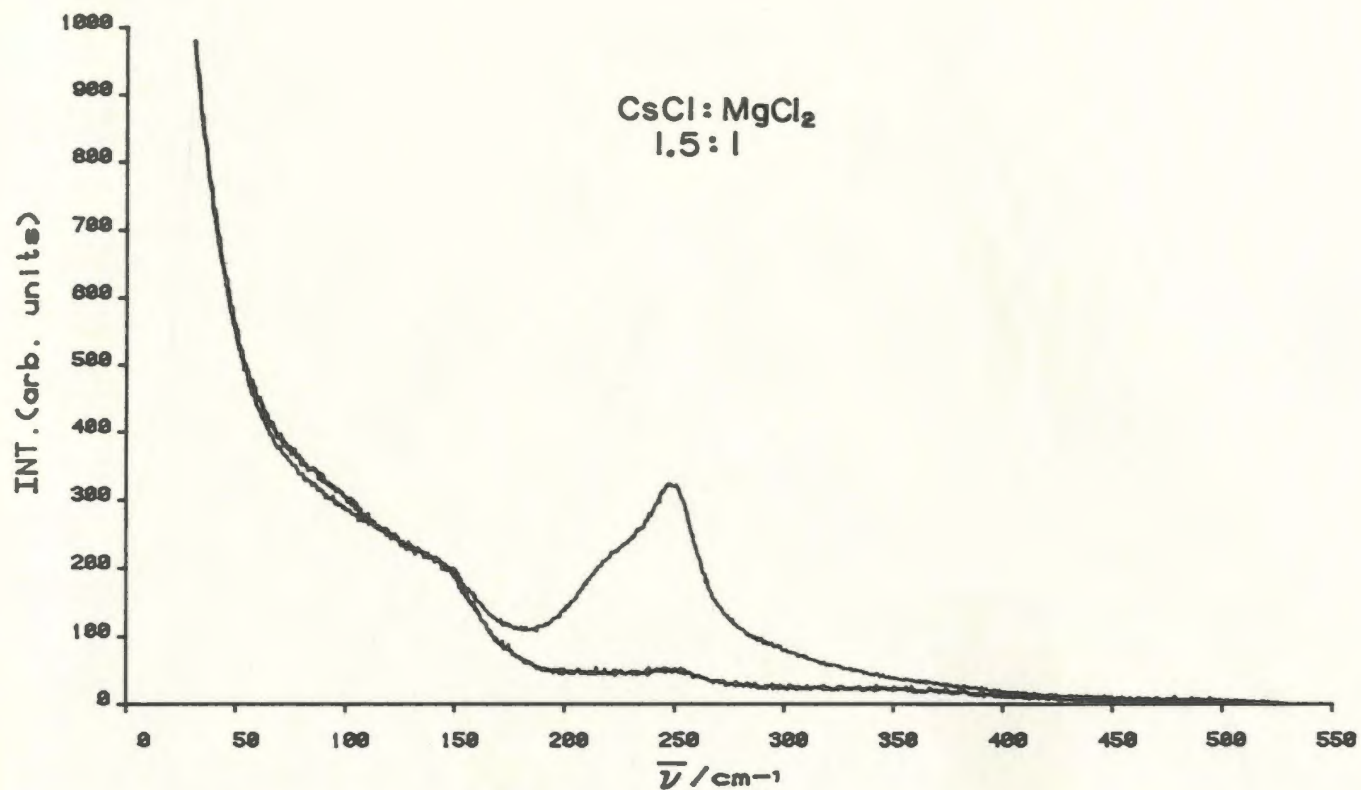




Figure 63. Raman spectra of molten  $\text{CsMgCl}_3$  at 896 K,

$I_{||}$  and  $I_{\perp}$ .

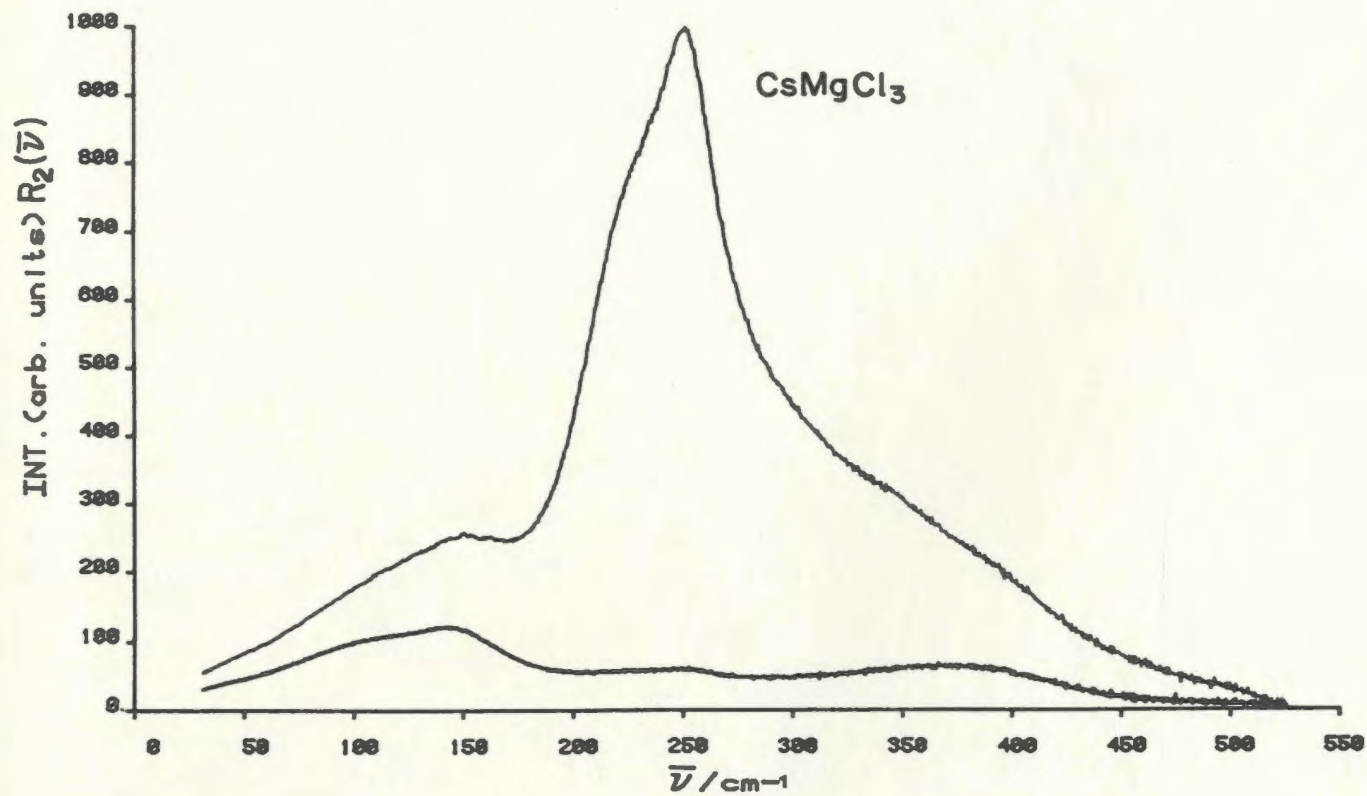
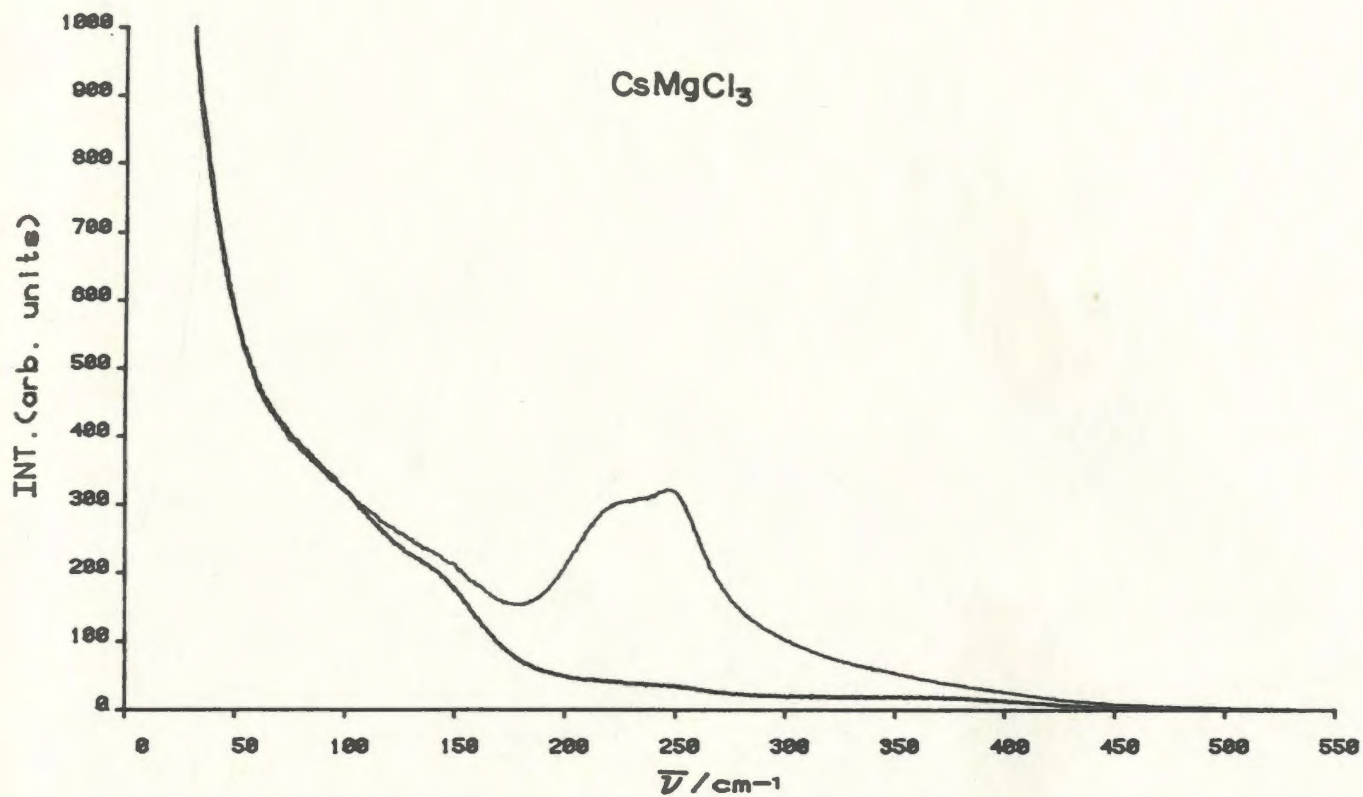


Figure 64. Raman spectra of molten  $\text{CsCl:MgCl}_2$  (0.5:1) at  
915 K,  $I_{||}$  and  $I_{\perp}$ .



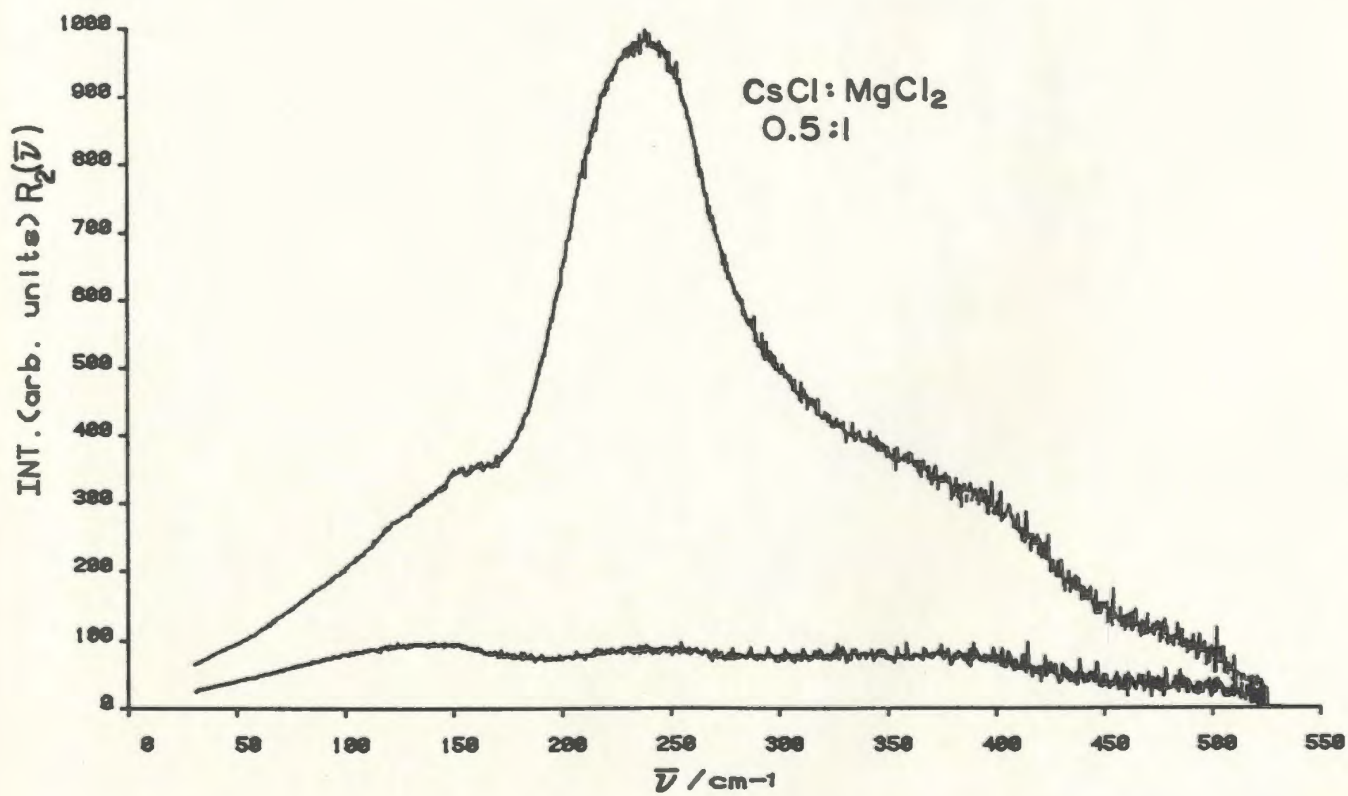
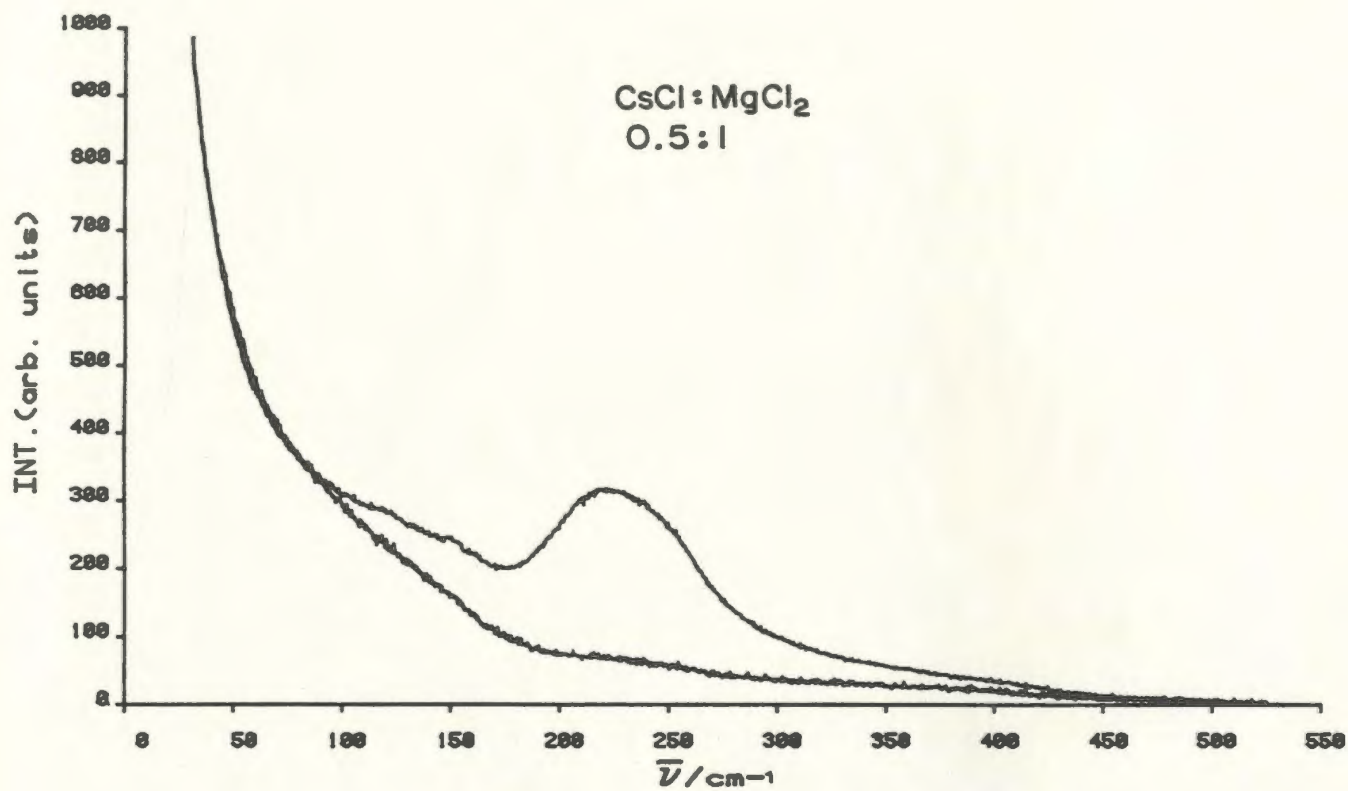


Figure 65. Raman spectra of molten  $\text{MgCl}_2$  at 1056 K,  $I_{||}$   
and  $I_{\perp}$ .

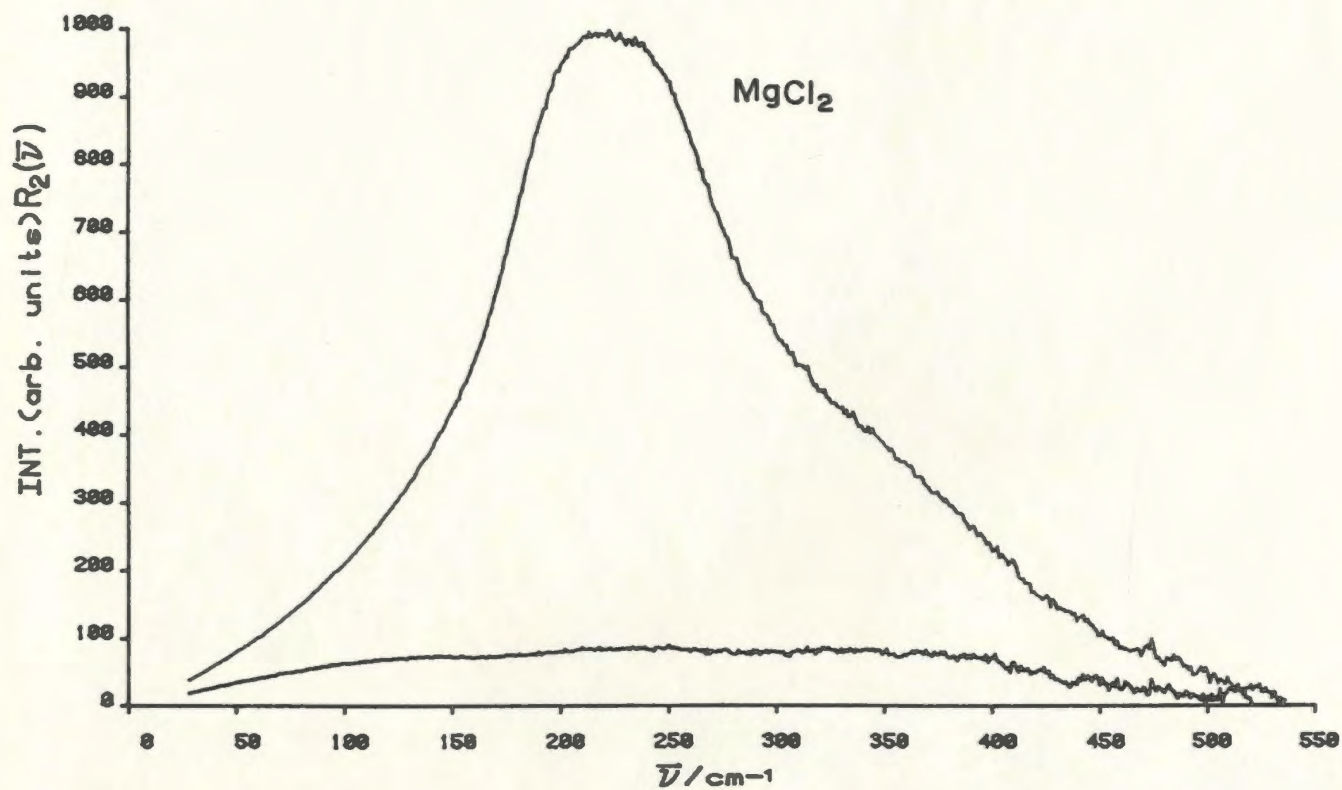
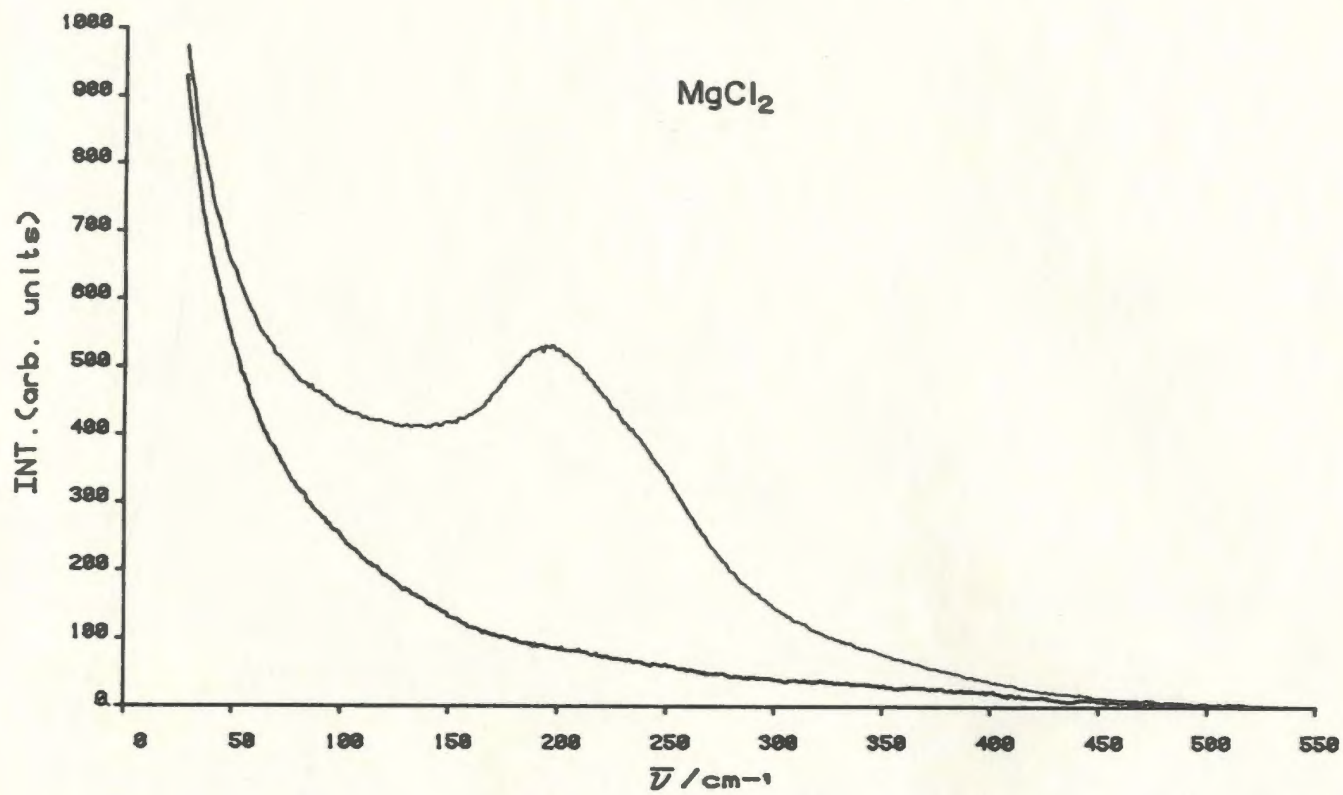




Figure 66. Isotropic Raman spectra of molten  $\text{CsCl:MgCl}_2$  (4:1).  
The smooth line is the best-fit curve calculated with  
a single Lorentzian function.

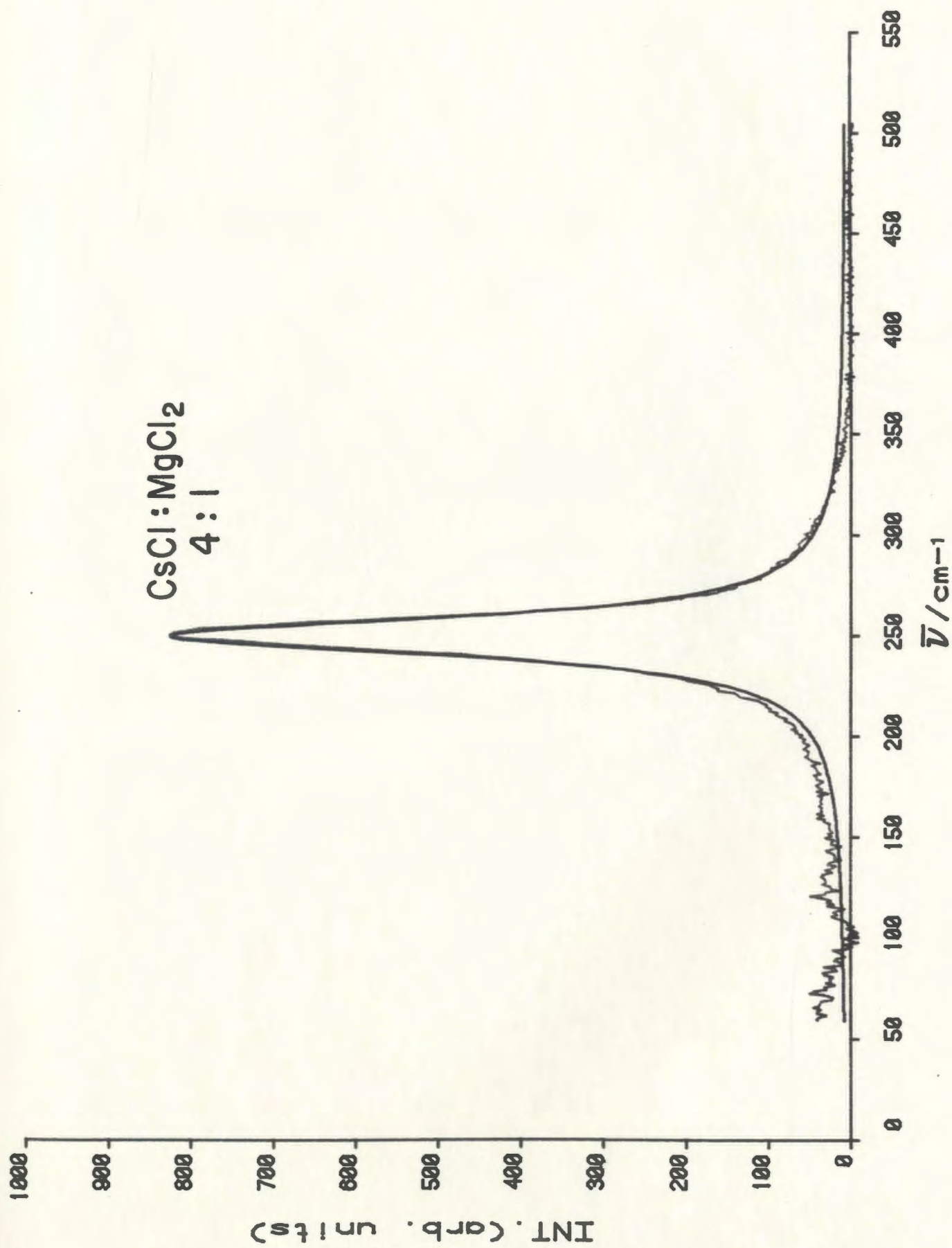


Figure 67. Isotropic Raman spectra of molten  $\text{Cs}_2\text{MgCl}_4$ .  
The smooth line is the best-fit curve calculated  
as a sum of three Lorentzian functions.



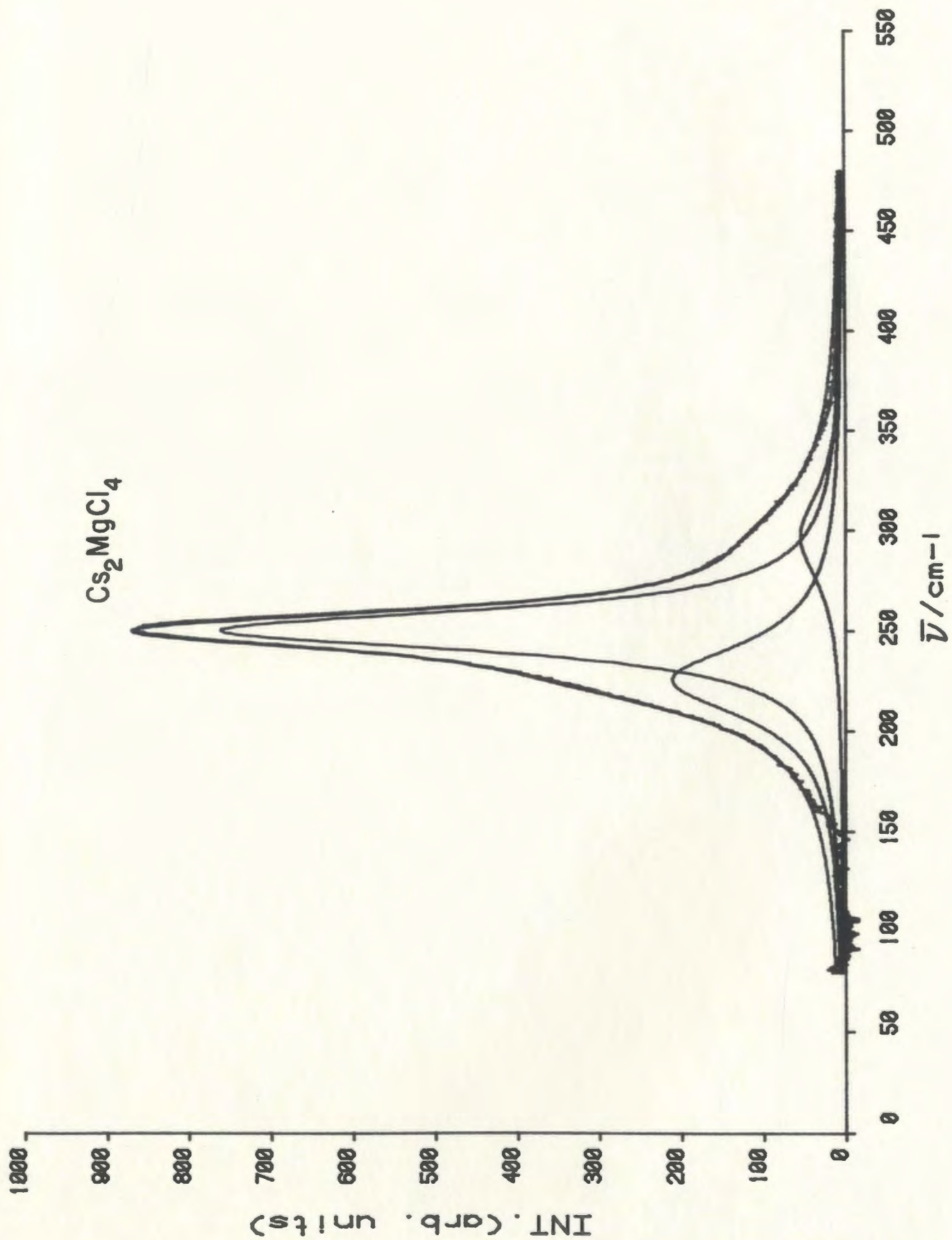


Figure 68. Isotropic Raman spectra of molten  $\text{CsCl:MgCl}_2$  (1.5:1). The smooth line is the best-fit curve calculated as a sum of three Lorentzian functions.

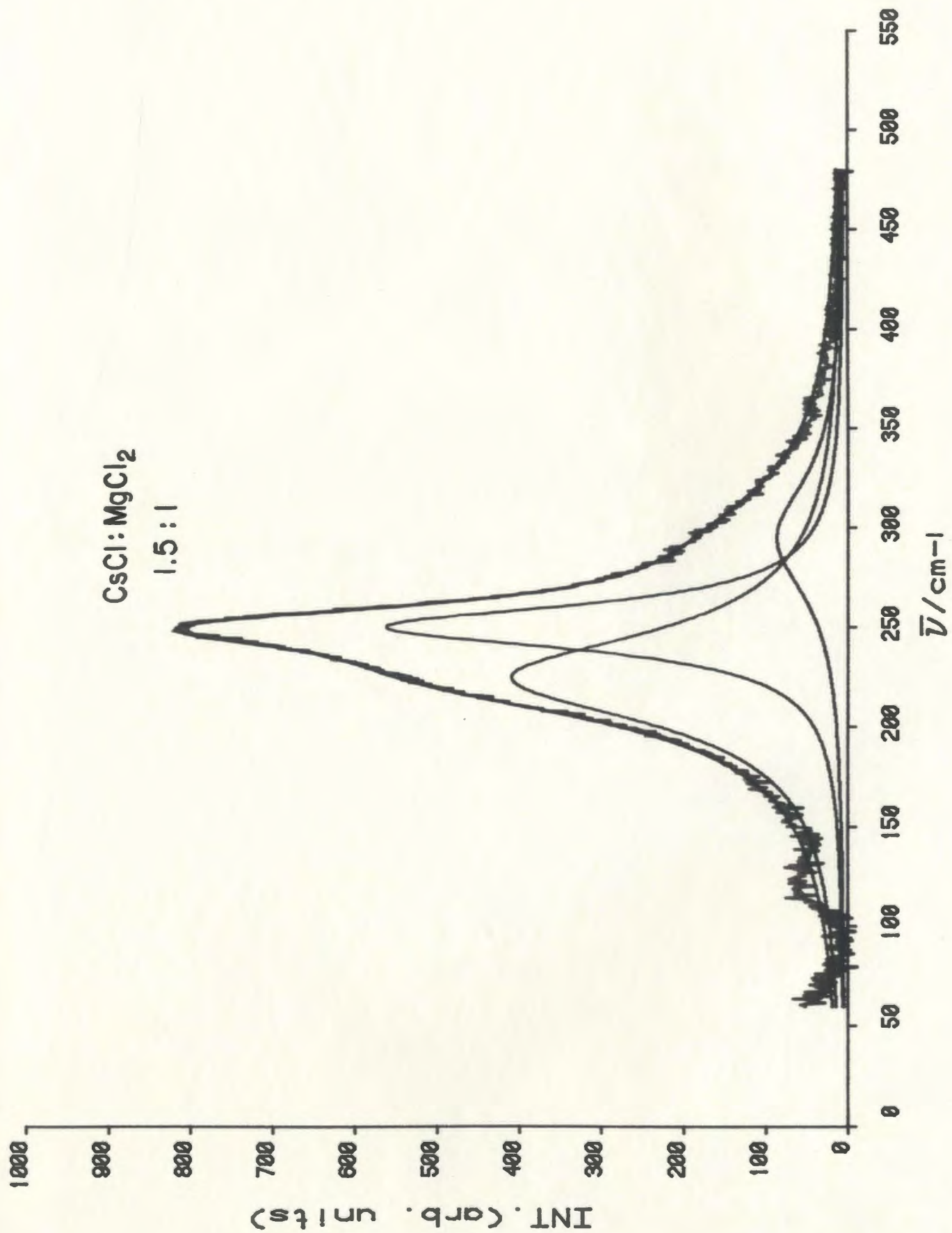




Figure 69. Isotropic Raman spectra of molten  $\text{CsMgCl}_3$ . The smooth line is the best-fit curve calculated as a sum of three Lorentzian functions.

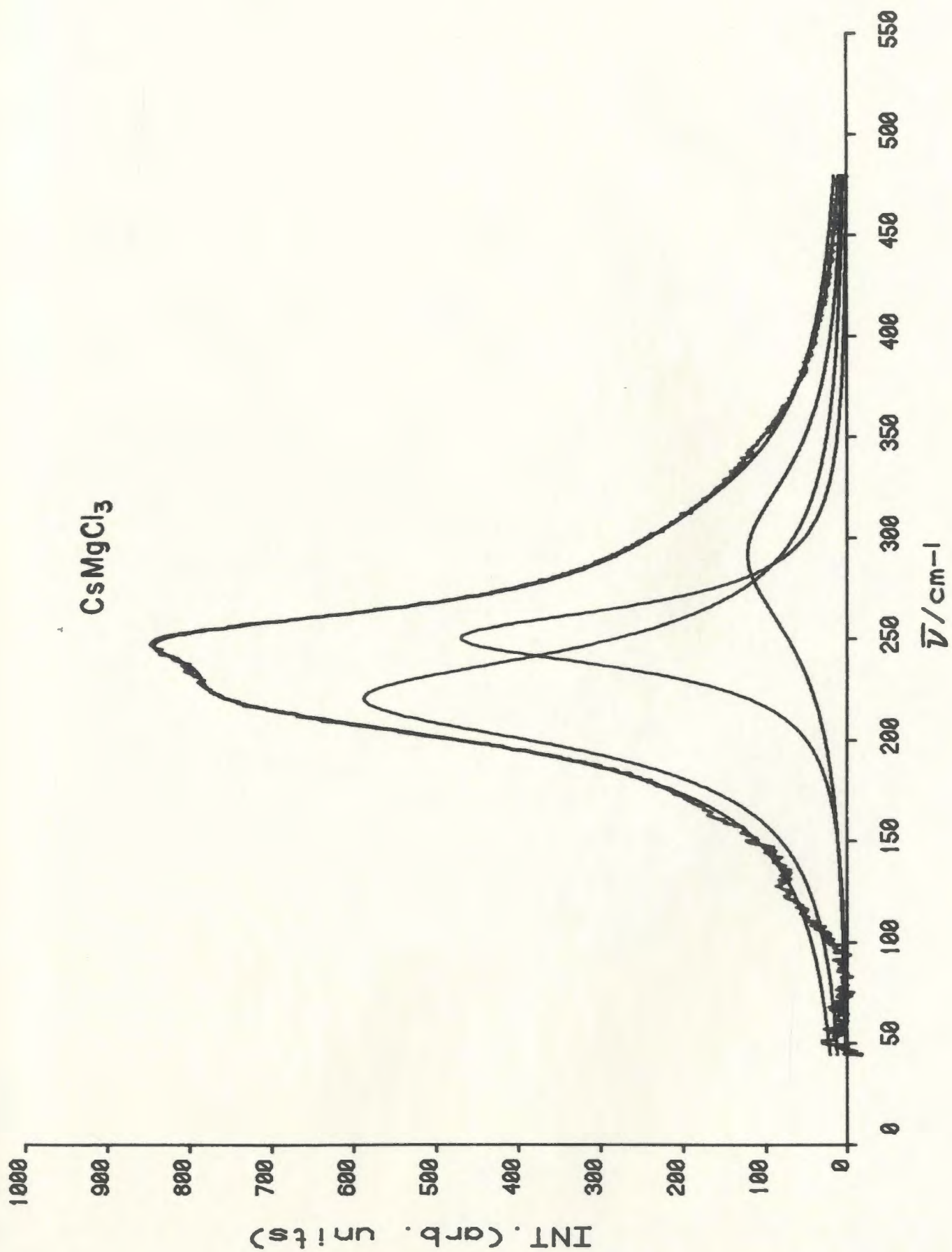


Figure 70. Isotropic Raman spectra of molten  $\text{CsCl:MgCl}_2$  (0.5:1). The smooth line is the best-fit curve calculated as a sum of four Lorentzian functions.



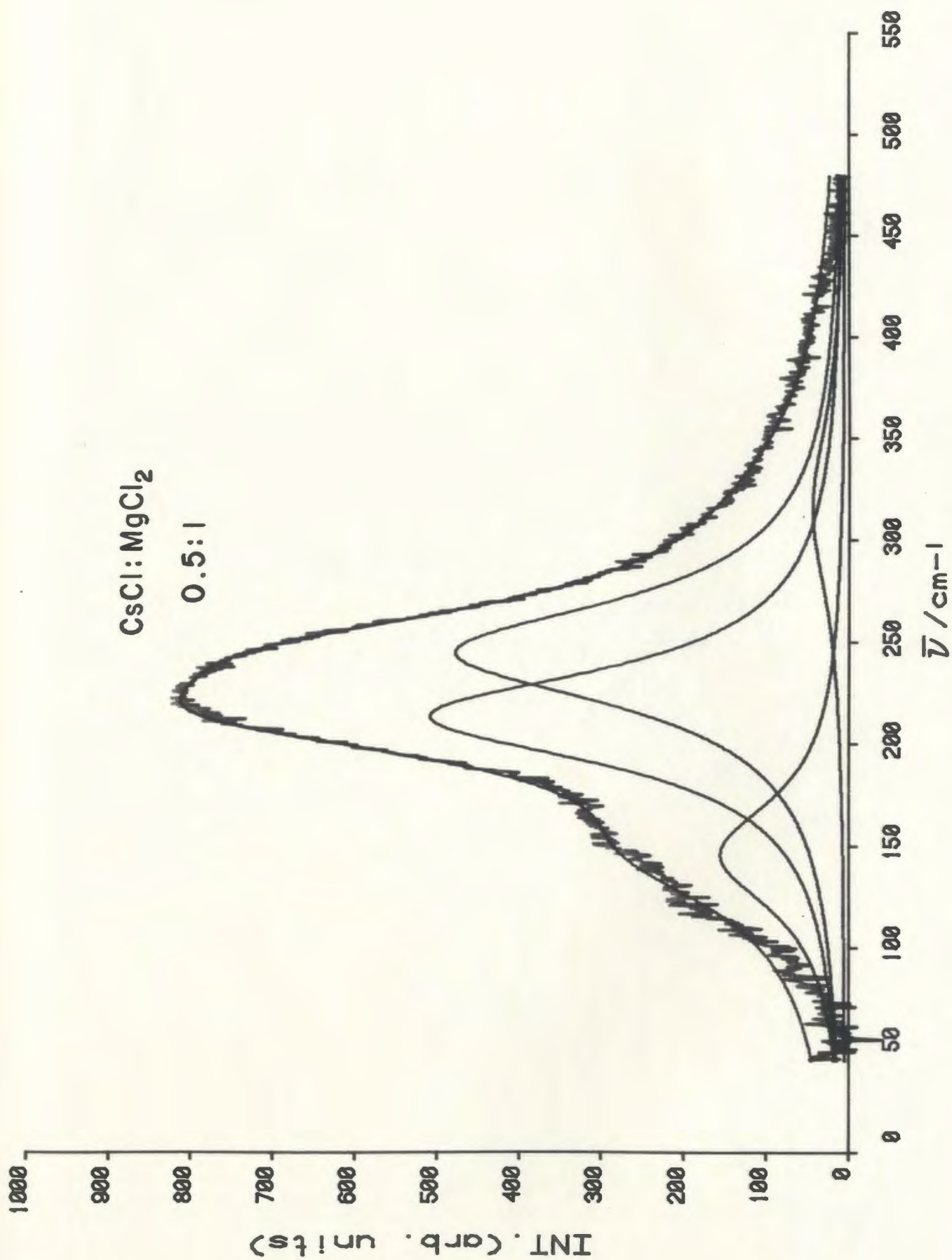
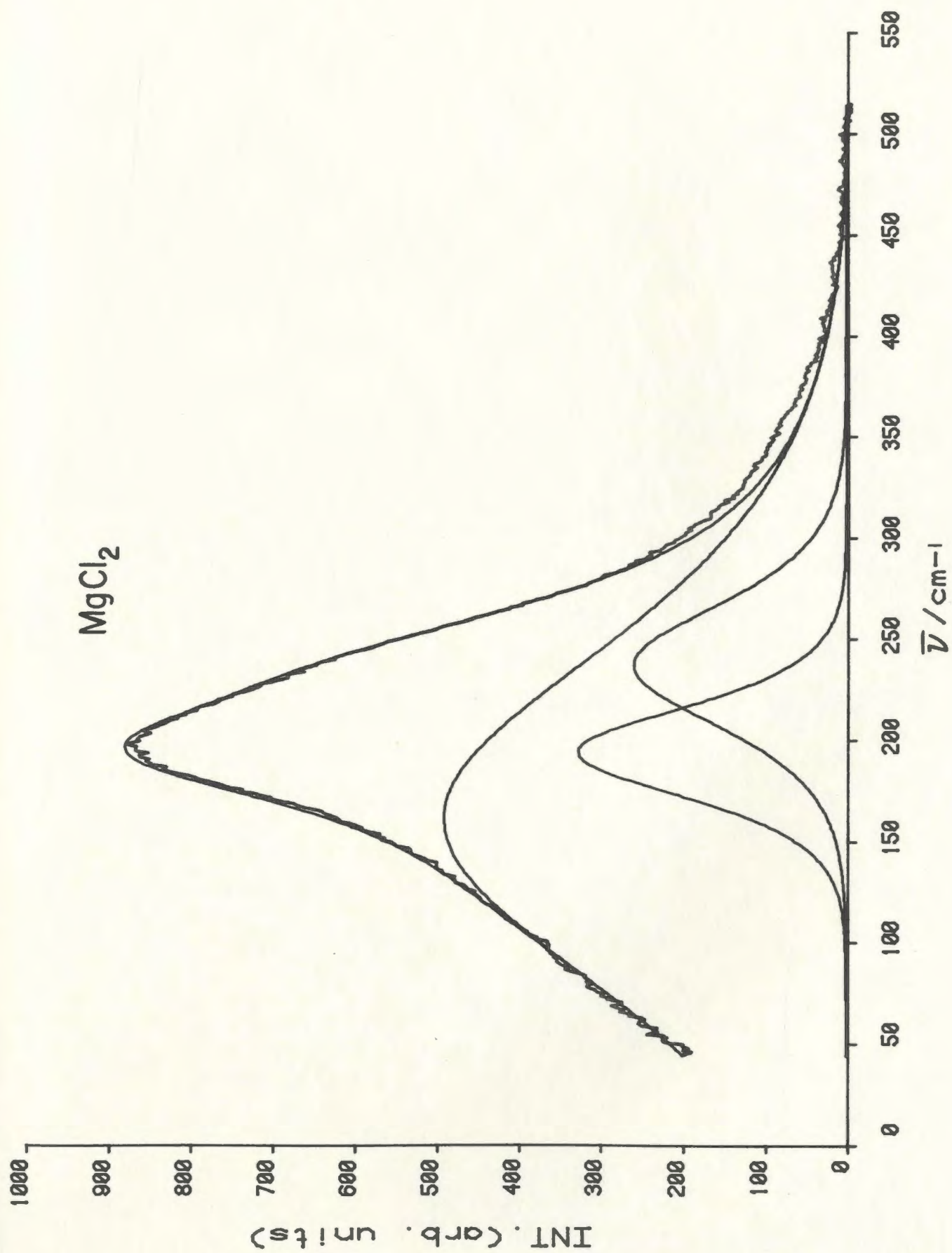


Figure 71. Isotropic Raman spectra of molten  $\text{MgCl}_2$ . The smooth line is the best-fit curve calculated as a sum of three Gaussian\*Lorentzian functions.





system the smaller  $K^+$  ion results in greater environmental broadening. The peak resolved around  $\sim 250 \text{ cm}^{-1}$  is attributed to the  $\nu_1$  mode of the  $\text{MgCl}_4^{2-}$  ions while the ones resolved around  $\sim 220$  and  $300 \text{ cm}^{-1}$  are attributed to the  $\text{Mg}_2\text{Cl}_7^{3-}$  ions. The polarized peak resolved at  $137 \text{ cm}^{-1}$  in  $\text{KCl:MgCl}_2$  (0.5:1) melt corresponds to the counterparts resolved at  $161$  and  $145 \text{ cm}^{-1}$  in  $\text{MgCl}_2$  and  $\text{CsCl:MgCl}_2$  (0.5:1) melts and attributed to polynuclear species of positive or neutral ions. The Raman data suggest that the  $\text{KCl:MgCl}_2$  (0.5:1) melt contains a mixture of  $\text{MgCl}_4^{2-}$  ions,  $\text{Mg}_2\text{Cl}_7^{3-}$  ions, and  $\text{Mg}_2\text{Cl}_n^{4-n}$  species. The synthetic and experimental spectra are shown in figures 76, 77, 78 and 79, and the curve resolution data are shown in Table 27.

#### 4.3.3. Effect of temperature on the spectra of $\text{CsMgCl}_3$ and $\text{K}_2\text{MgCl}_4$ Melts

It was reported<sup>14</sup> that the intensity of the polarized peak, estimated at  $225 \text{ cm}^{-1}$  and attributed to polynuclear species, decreased by increasing the temperature i.e. the intensity ratio  $I_{225}/I_{250}$  is decreasing by increasing the temperature. This decrease in intensity ratio by increasing the temperature was attributed to the breaking of the polynuclear species and the formation of more  $\text{MgCl}_4^{2-}$  species.

The spectra of  $\text{CsMgCl}_3$  melt were obtained at 899, 1054 and 1153 K, and it appears that the intensity of the peak due to  $\text{Mg}_2\text{Cl}_7^{3-}$  ions does decrease with increasing the temperature, see figures 80, 81 and 82, Table 28. The spectra of  $\text{K}_2\text{MgCl}_4$  melt are studied at 973 and 1143 K. Again the data indicate the breaking of the polynuclear species and the formation of more  $\text{MgCl}_4^{2-}$  ions. The spectra are shown in figures 83 and 84. The results of the curve resolution analysis for  $\text{CsMgCl}_3$  and  $\text{K}_2\text{MgCl}_4$  at different temperatures are shown in Table 28.

Table 27. Summary of results of curve resolution analysis for  
MgCl<sub>2</sub>-KCl Melts.

Compound	Frequency (cm <sup>-1</sup> )	Intensity	Half band width (cm <sup>-1</sup> )	Assignments
K <sub>2</sub> MgCl <sub>4</sub>	219.4	132	50.1	(ν) Mg <sub>2</sub> Cl <sub>7</sub> <sup>3-</sup>
	247.5	357	40.4	(ν <sub>1</sub> ) MgCl <sub>4</sub> <sup>2-</sup>
	296.3	21	44.8	(ν) Mg <sub>2</sub> Cl <sub>7</sub> <sup>3-</sup>
KCl:MgCl <sub>2</sub> (1.5:1)	227.9	361	93.5	(ν) Mg <sub>2</sub> Cl <sub>7</sub> <sup>3-</sup>
	248.5	194	46.4	(ν <sub>1</sub> ) MgCl <sub>4</sub> <sup>2-</sup>
	299.4	33	61.9	(ν) Mg <sub>2</sub> Cl <sub>7</sub> <sup>3-</sup>
KMgCl <sub>3</sub>	220.7	276	77.2	(ν) Mg <sub>2</sub> Cl <sub>7</sub> <sup>3-</sup>
	249.4	123	44.9	(ν <sub>1</sub> ) MgCl <sub>4</sub> <sup>2-</sup>
	293.1	24	81.7	(ν) Mg <sub>2</sub> Cl <sub>7</sub> <sup>3-</sup>
KCl:MgCl <sub>2</sub> (0.5:1)	137.8	96	236.7	(ν) polynuclear species
	212.9	216	60.6	(ν) Mg <sub>2</sub> Cl <sub>7</sub> <sup>3-</sup>
	244.2	218	69.1	(ν <sub>1</sub> ) MgCl <sub>4</sub> <sup>2-</sup>
	295.0	5	20.0	(ν) Mg <sub>2</sub> Cl <sub>7</sub> <sup>3-</sup>

Figure 72. Raman spectra of molten  $\text{K}_2\text{MgCl}_4$  at 1049 K,

$I_{||}$  and  $I_{\perp}$ .



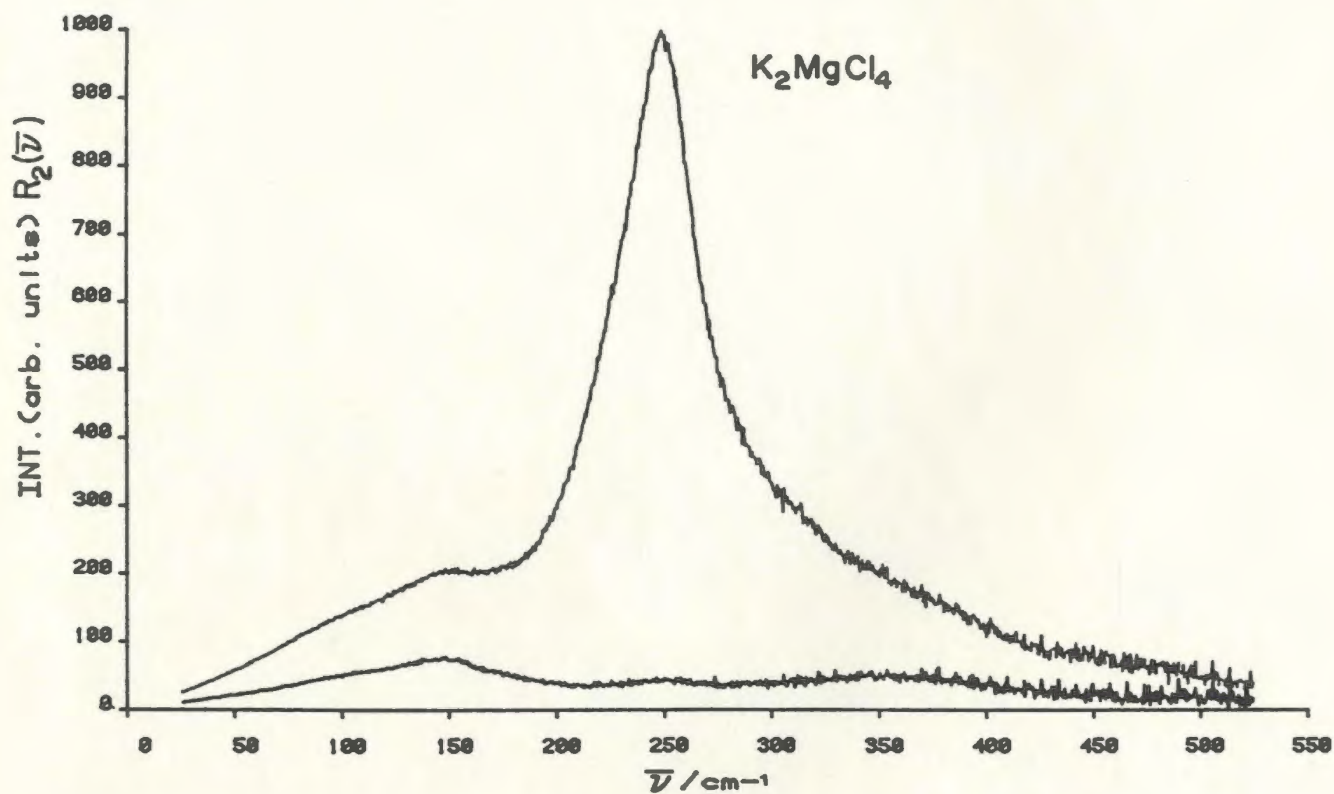
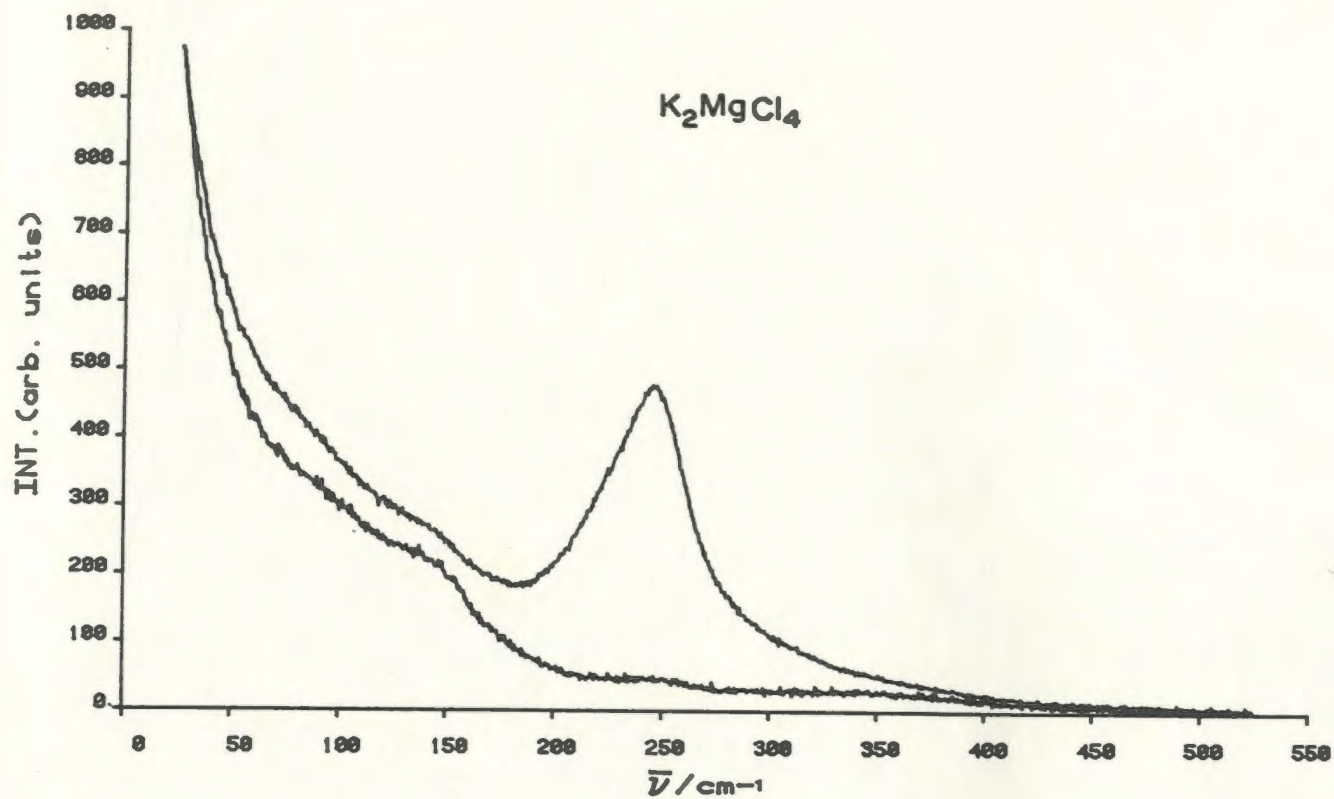


Figure 73. Raman spectra of molten  $\text{KCl:MgCl}_2$  (1.5:1) at  
1049 K,  $I_{||}$  and  $I_{\perp}$ .

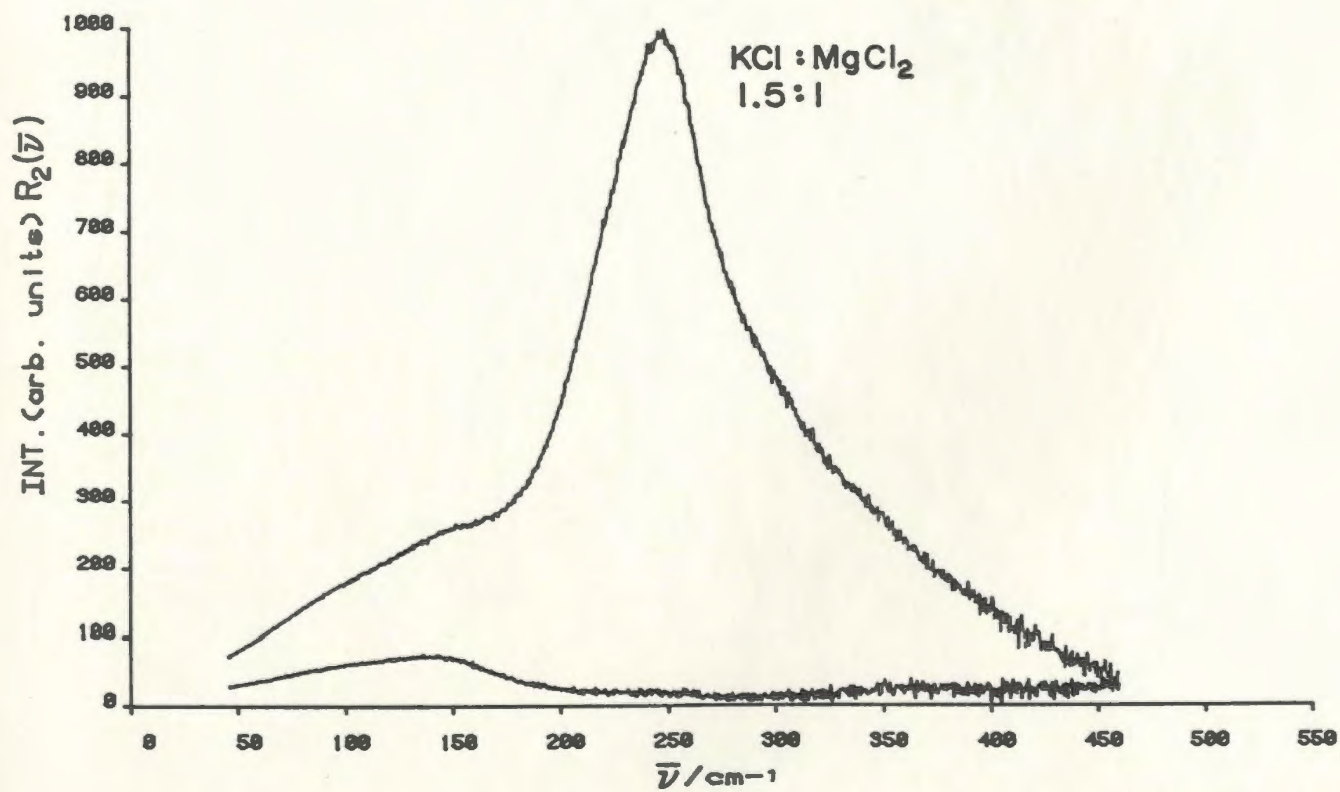
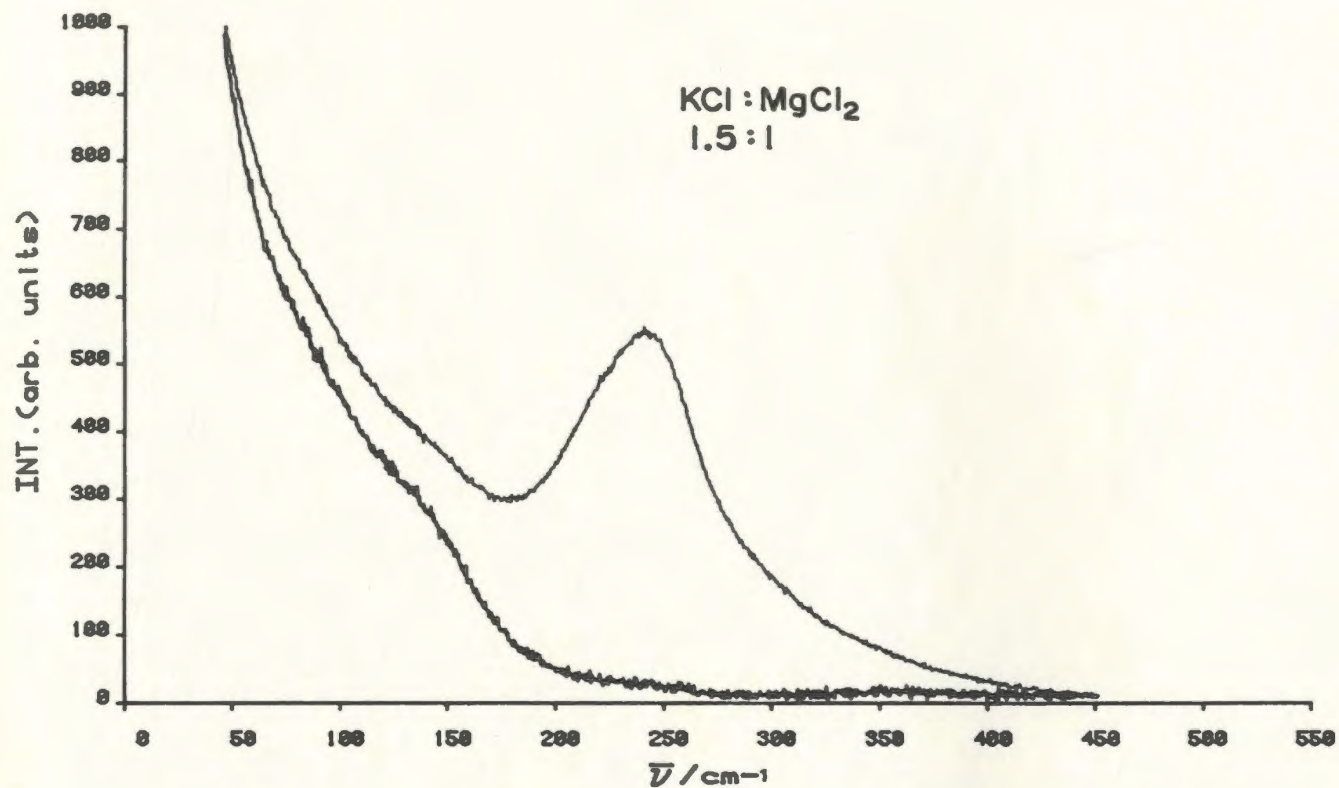




Figure 74. Raman spectra of molten  $\text{KMgCl}_3$  at 1049 K,

$I_{||}$  and  $I_{\perp}$ .

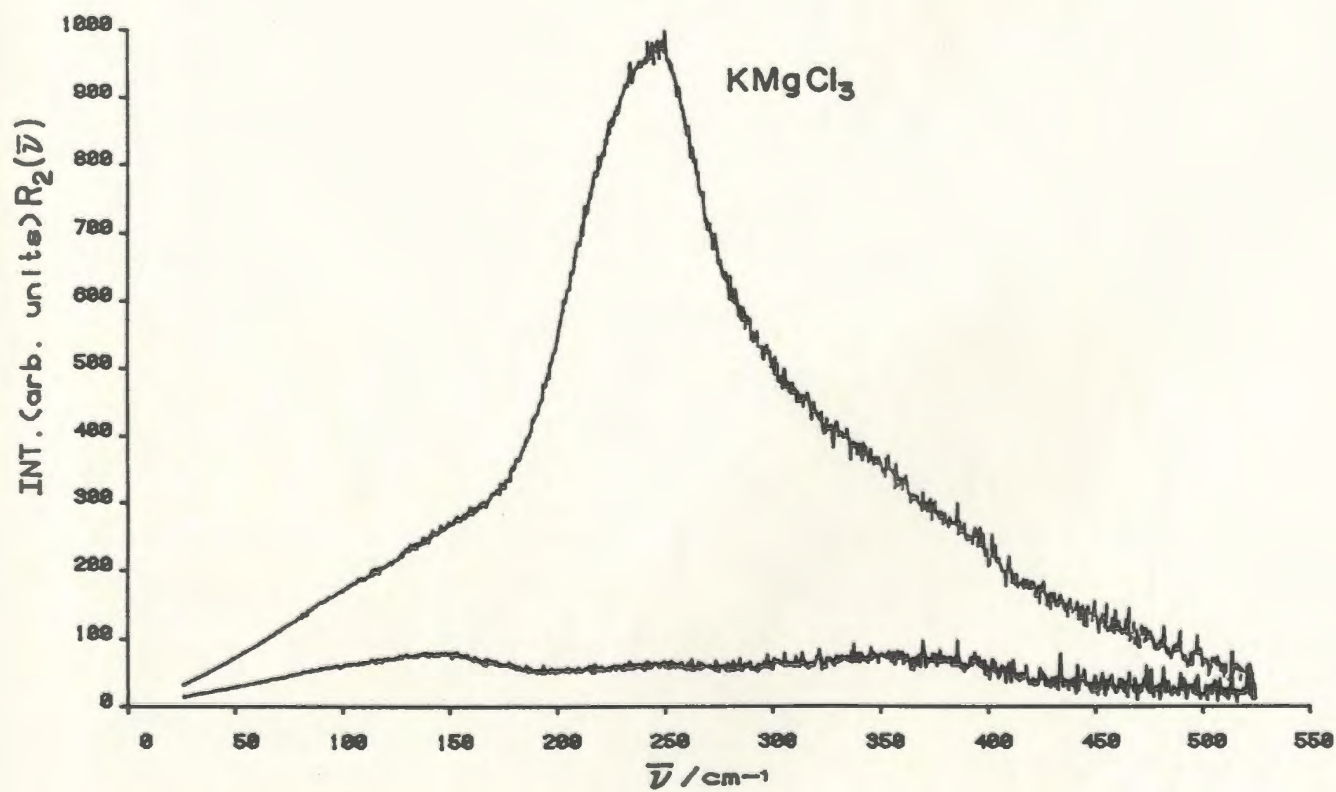
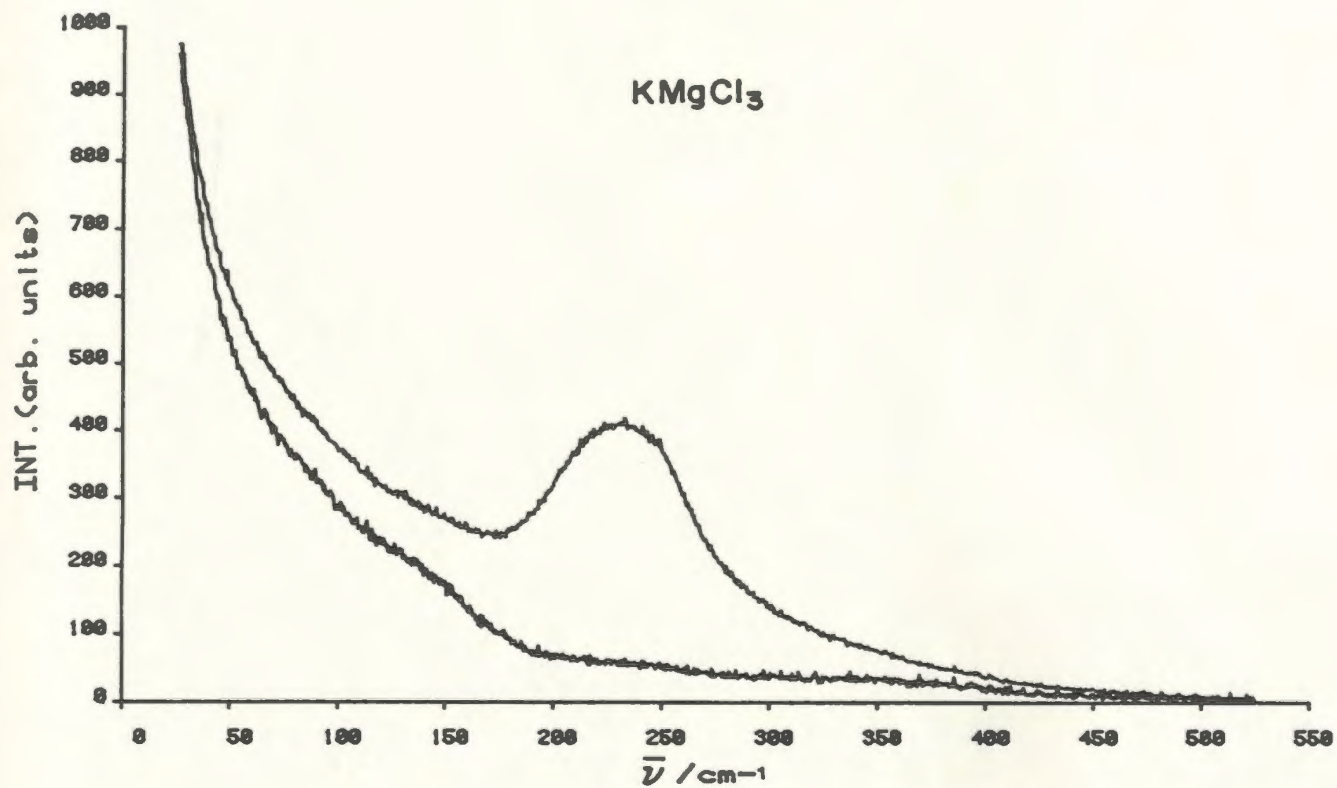


Figure 75. Raman spectra of molten  $\text{KCl:MgCl}_2$  (0.5:1) at  
1049 K,  $I_{||}$  and  $I_{\perp}$ .



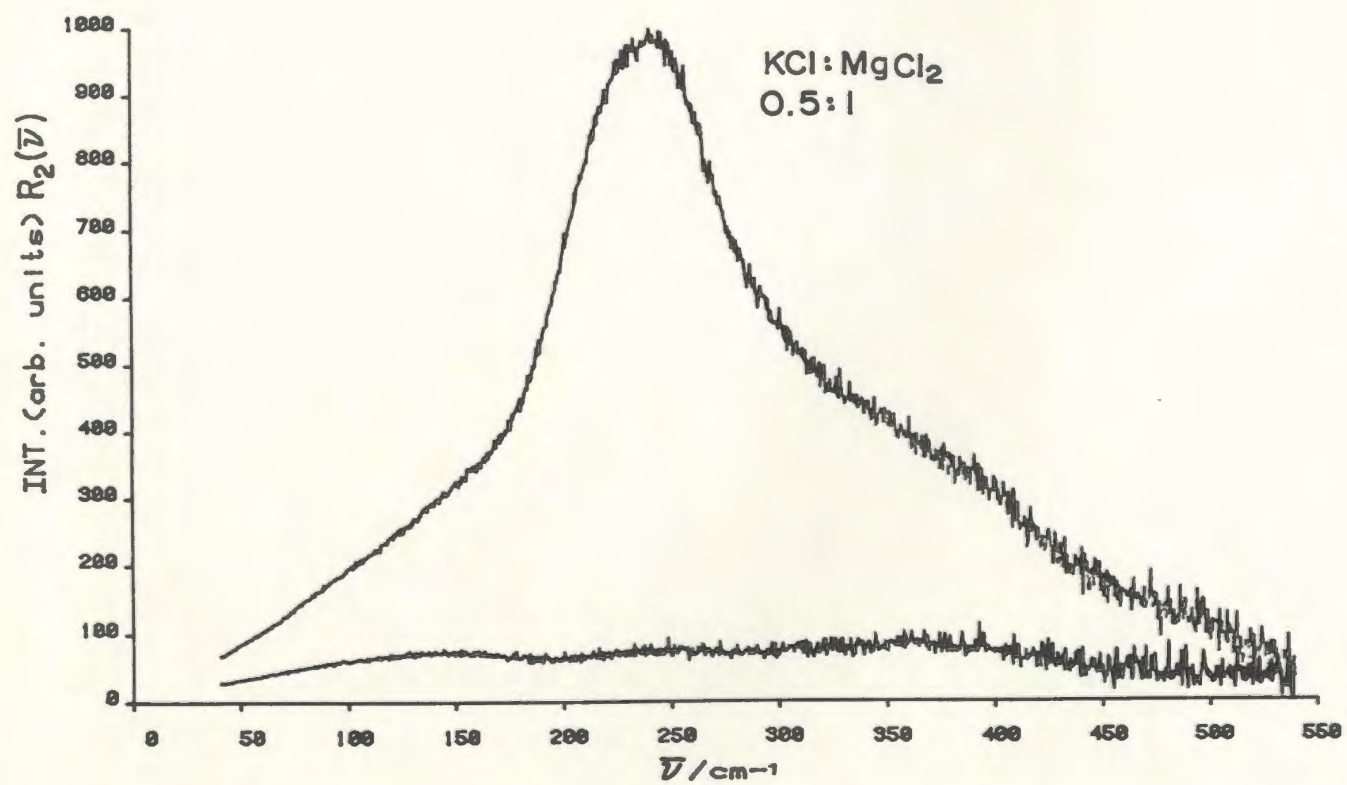
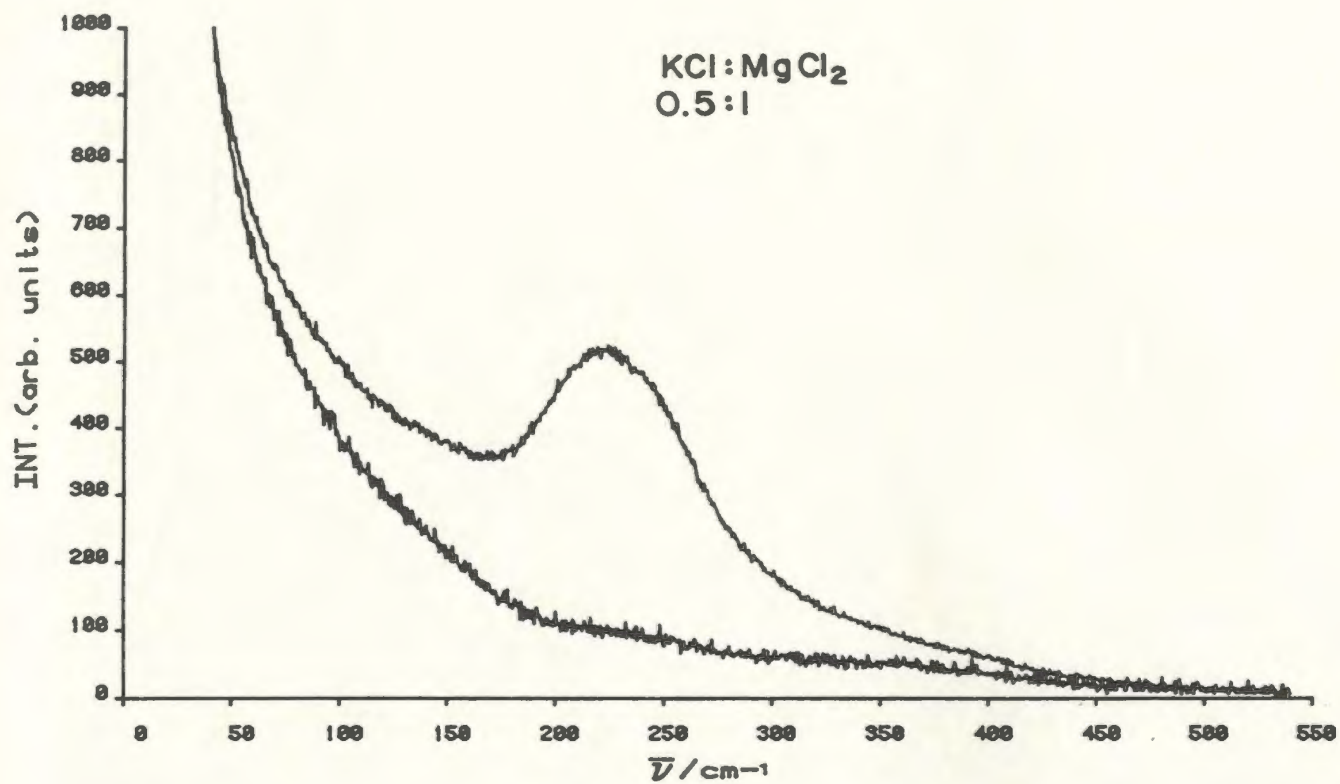


Figure 76. Isotropic Raman spectra of molten  $\text{K}_2\text{MgCl}_4$ . The smooth line is the best-fit curve calculated as a sum of three Lorentzian functions.

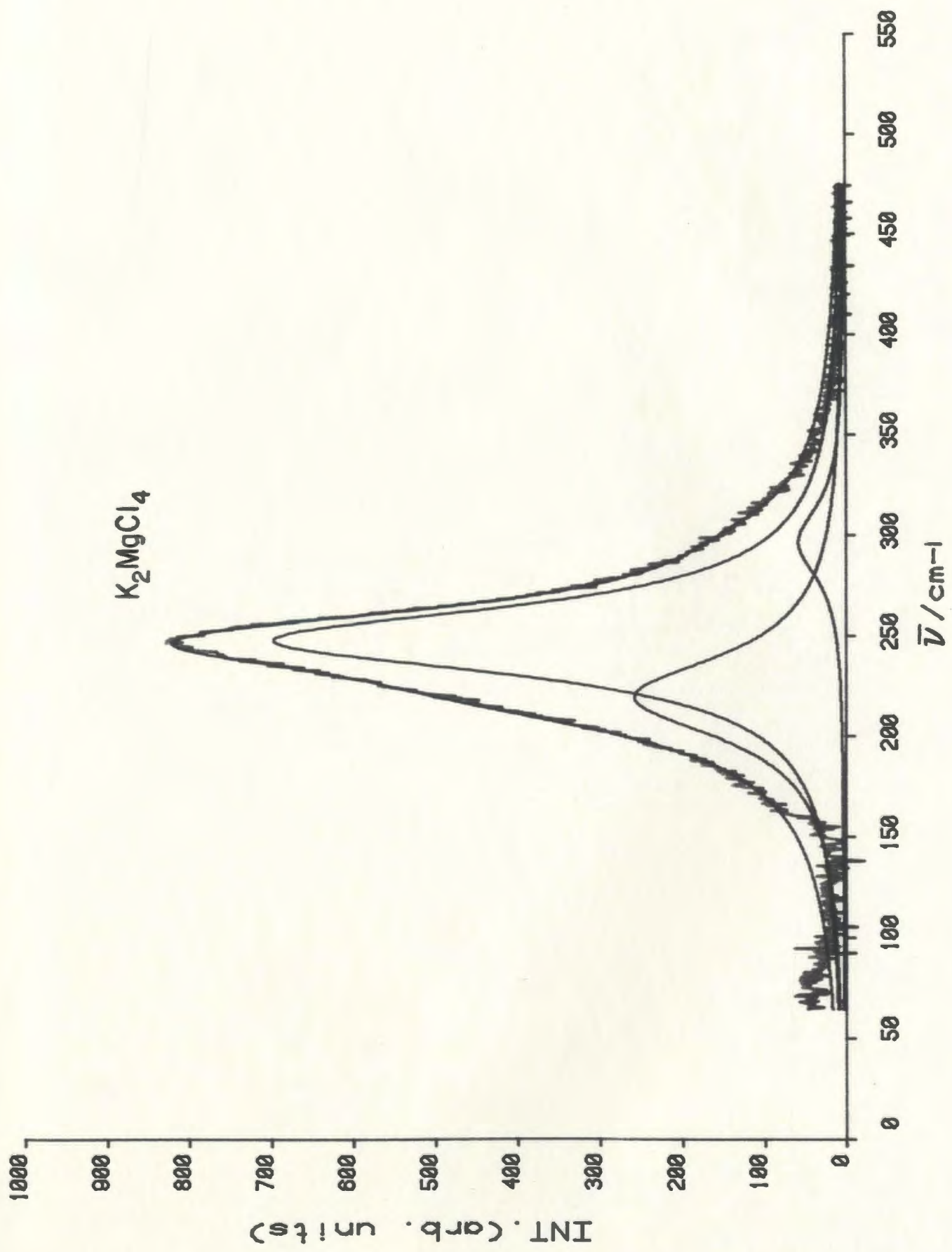




Figure 77. Isotropic Raman spectra of molten  $\text{KCl:MgCl}_2$  (1.5:1).  
The smooth line is the best-fit curve calculated as  
a sum of three Lorentzian functions.

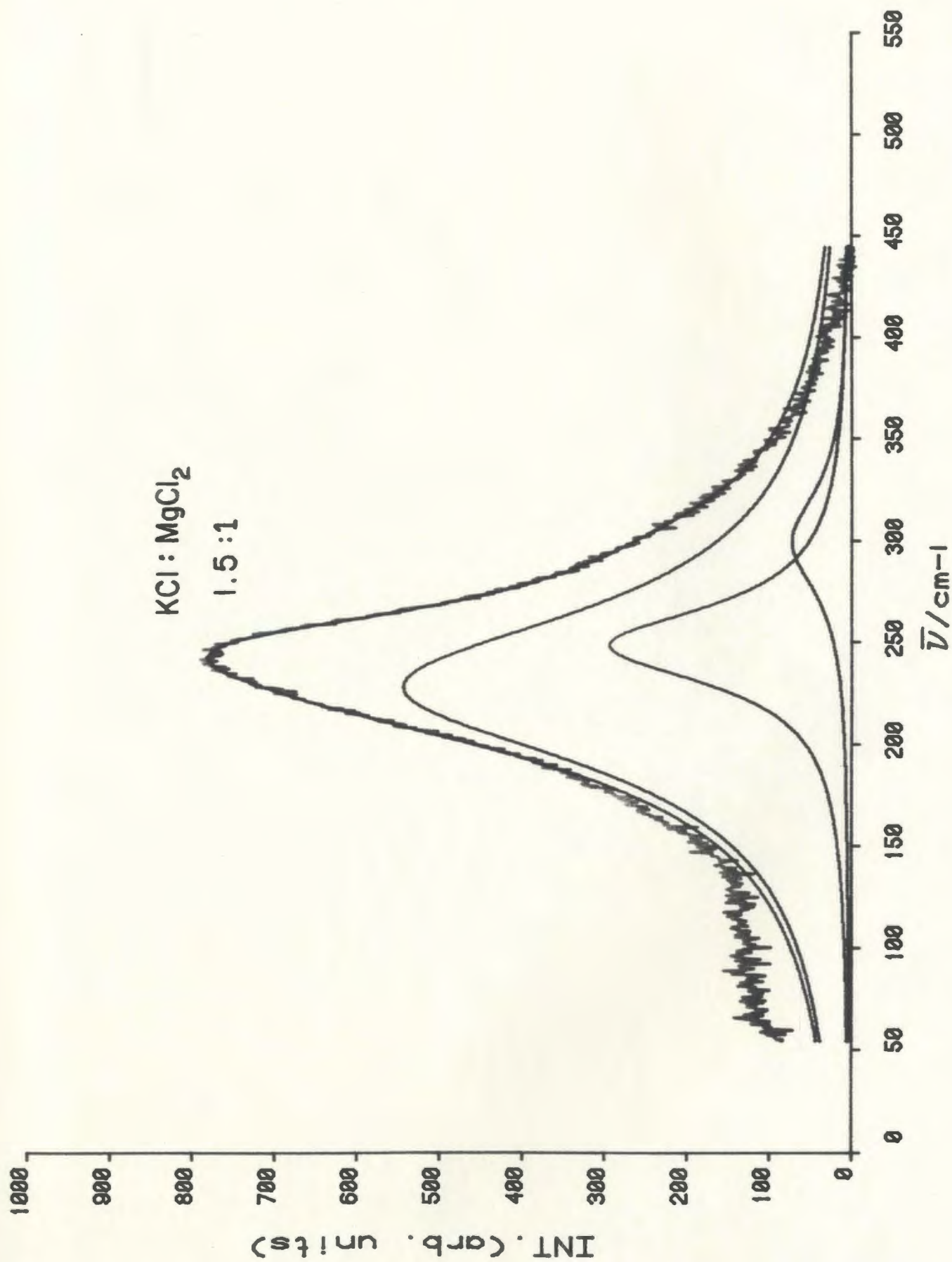


Figure 78. Isotropic Raman spectra of molten  $\text{KMgCl}_3$ . The smooth line is the best-fit curve calculated as a sum of three Lorentzian functions.



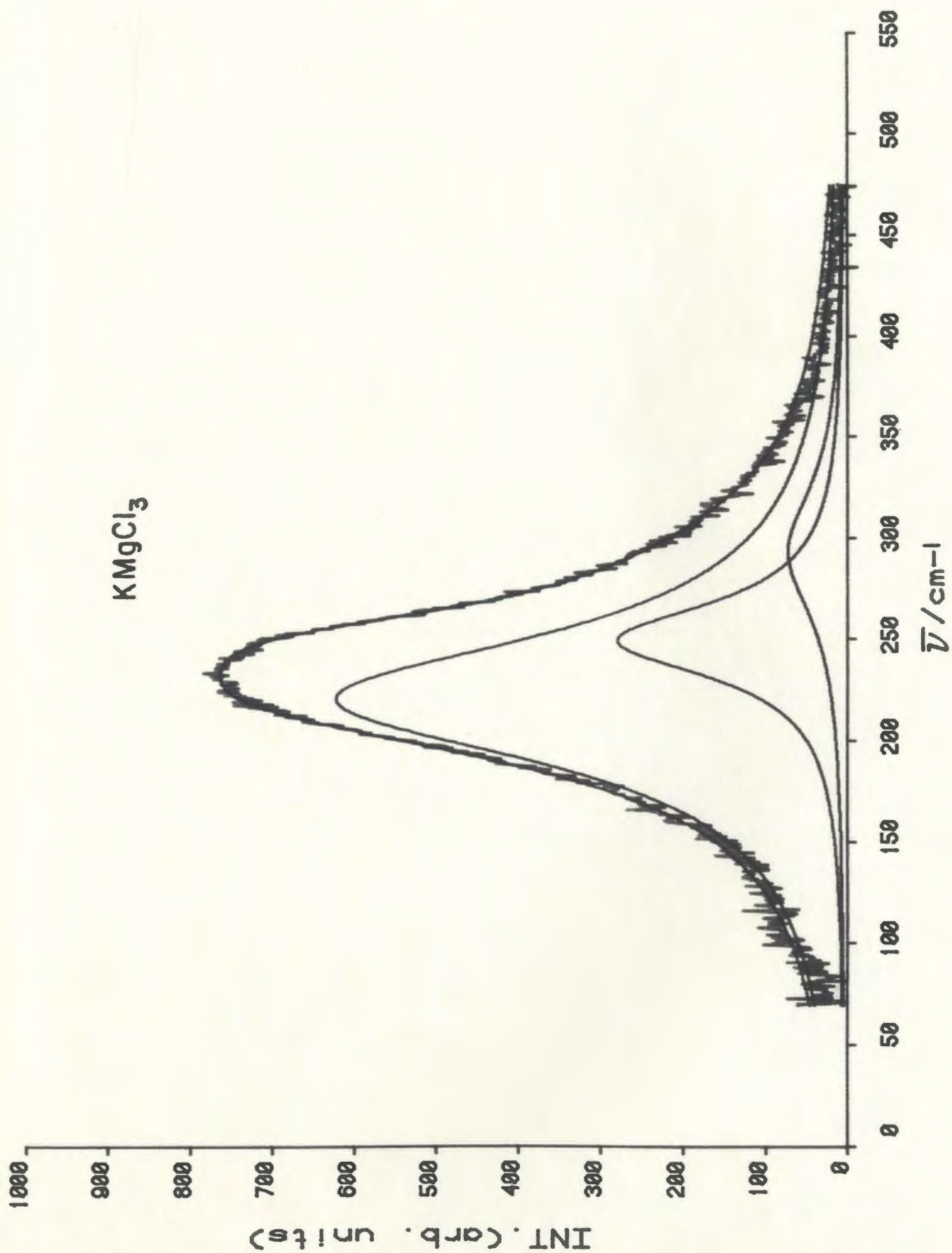


Figure 79. Isotropic Raman spectra of molten  $\text{KCl:MgCl}_2$  (0.5:1).  
The smooth line is the best-fit curve calculated as  
a sum of four Lorentzian functions.

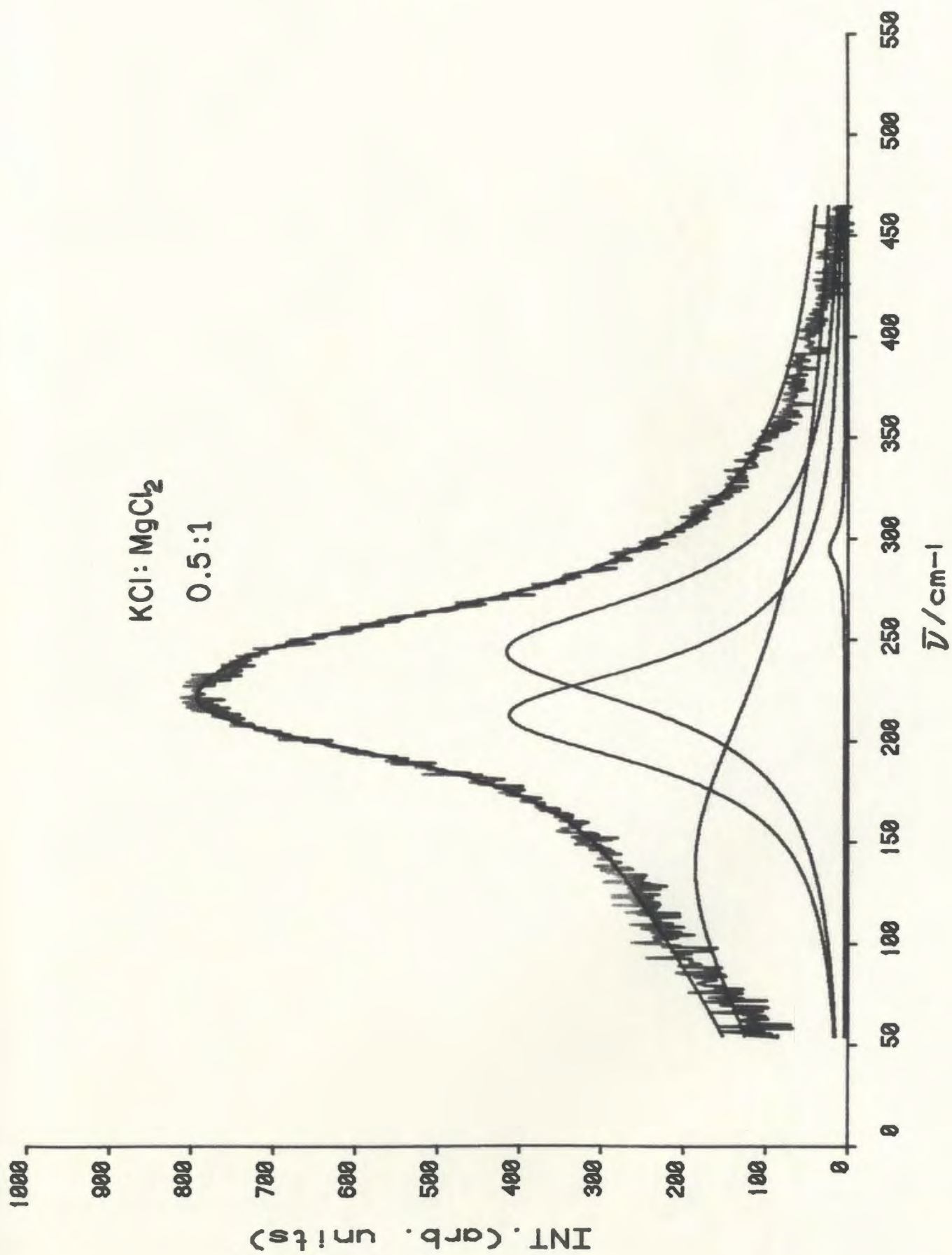




Table 28. Summary of results of curve resolution analysis for  $\text{CsMgCl}_3$  and  $\text{K}_2\text{MgCl}_4$  Melts.

Compound	Temperature (K)	Frequency ( $\text{cm}^{-1}$ )	Intensity	Half band width ( $\text{cm}^{-1}$ )	Intensity ratio
$\text{CsMgCl}_3$	899	216.6	241	61.5	$\frac{I_{216} \times \Gamma_{216}}{I_{247} \times \Gamma_{247}}$ = 1.98
		247.7	178	42.1	
	1054	212.5	181	63.9	$\frac{I_{212} \times \Gamma_{212}}{I_{245} \times \Gamma_{245}}$ = 1.26
		245.5	178	51.5	
	1153	209.0	124	63.0	$\frac{I_{209} \times \Gamma_{209}}{I_{243} \times \Gamma_{243}}$ = 0.84
		243.3	161	58.1	
$\text{K}_2\text{MgCl}_4$	973	225.3	146	54.7	$\frac{I_{225} \times \Gamma_{225}}{I_{249} \times \Gamma_{249}}$ = 0.72
		249.1	323	34.3	
	1143	218.7	54	69.1	$\frac{I_{218} \times \Gamma_{218}}{I_{246} \times \Gamma_{246}}$ = 0.68
		246.4	121	45.3	

Figure 80. Isotropic Raman spectra of molten  $\text{CsMgCl}_3$  at 899 K.  
The smooth line is the best-fit curve calculated as  
a sum of three Lorentzian functions.

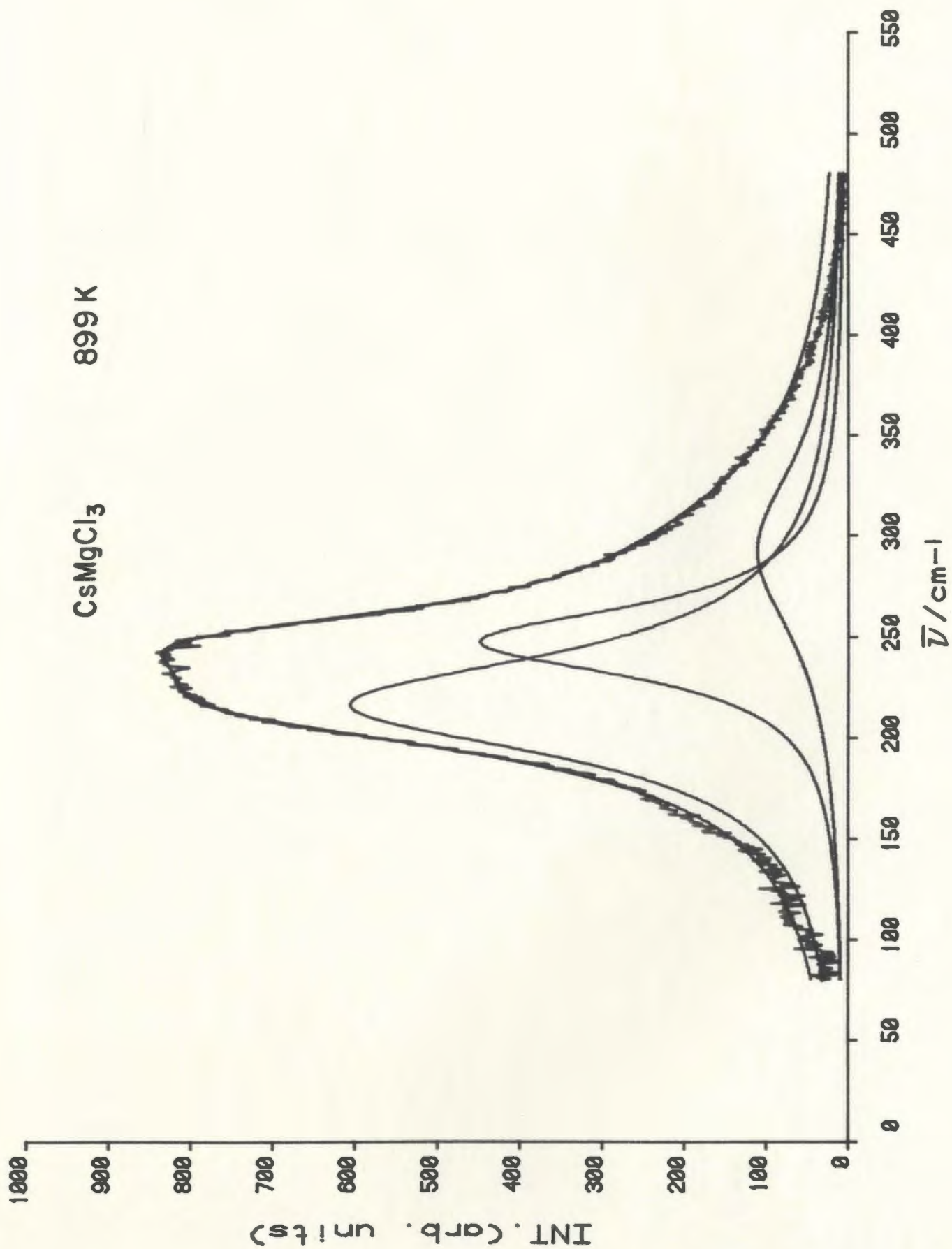




Figure 81. Isotropic Raman spectra of molten  $\text{CsMgCl}_3$  at 1054 K.  
The smooth line is the best-fit curve calculated as  
a sum of three Lorentzian functions.

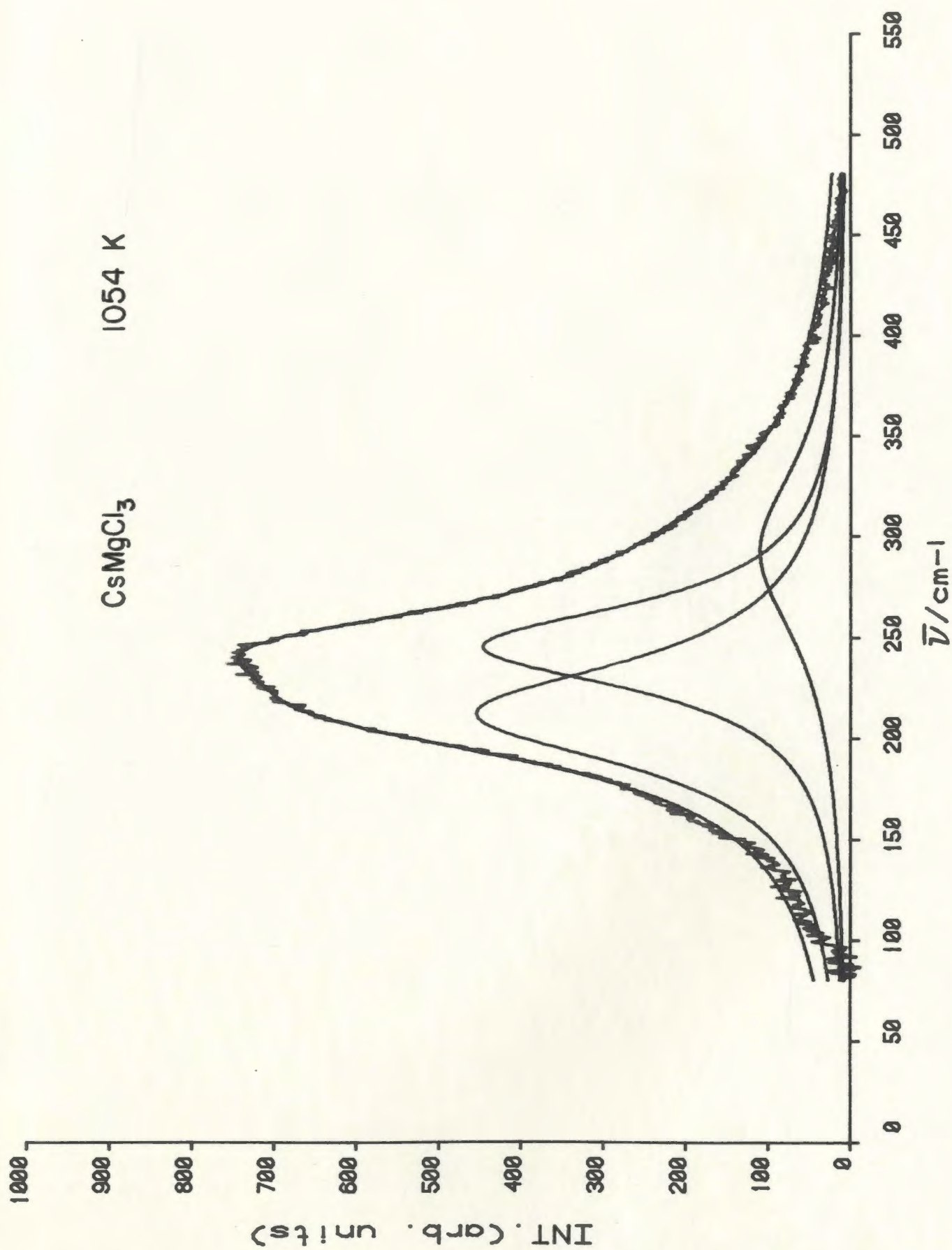


Figure 82. Isotropic Raman spectra of molten  $\text{CsMgCl}_3$  at 1153 K.  
The smooth line is the best-fit curve calculated as  
a sum of three Lorentzian functions.



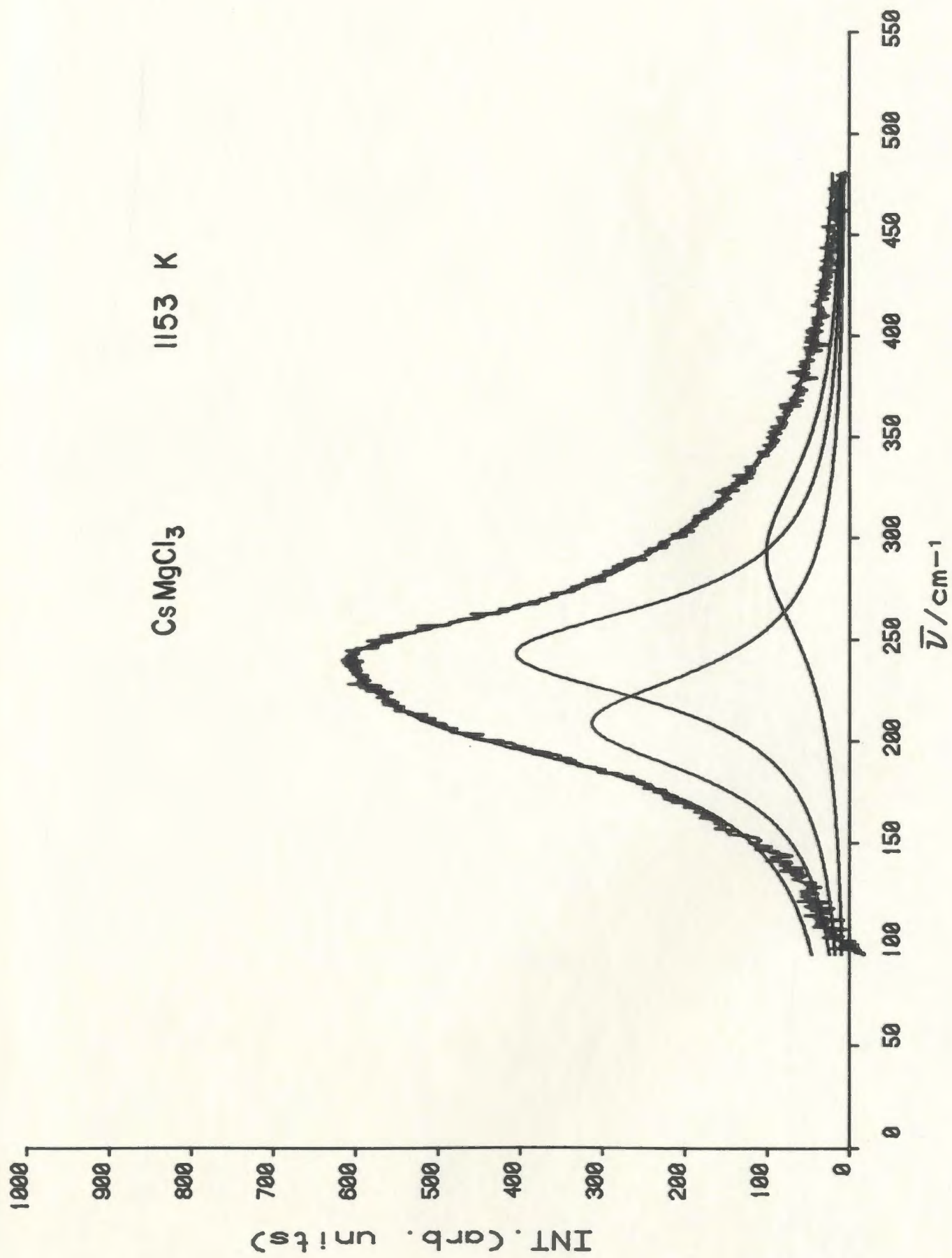


Figure 83. Isotropic Raman spectra of molten  $\text{K}_2\text{MgCl}_4$  at 973 K.  
The smooth line is the best-fit curve calculated as  
a sum of three Lorentzian functions.

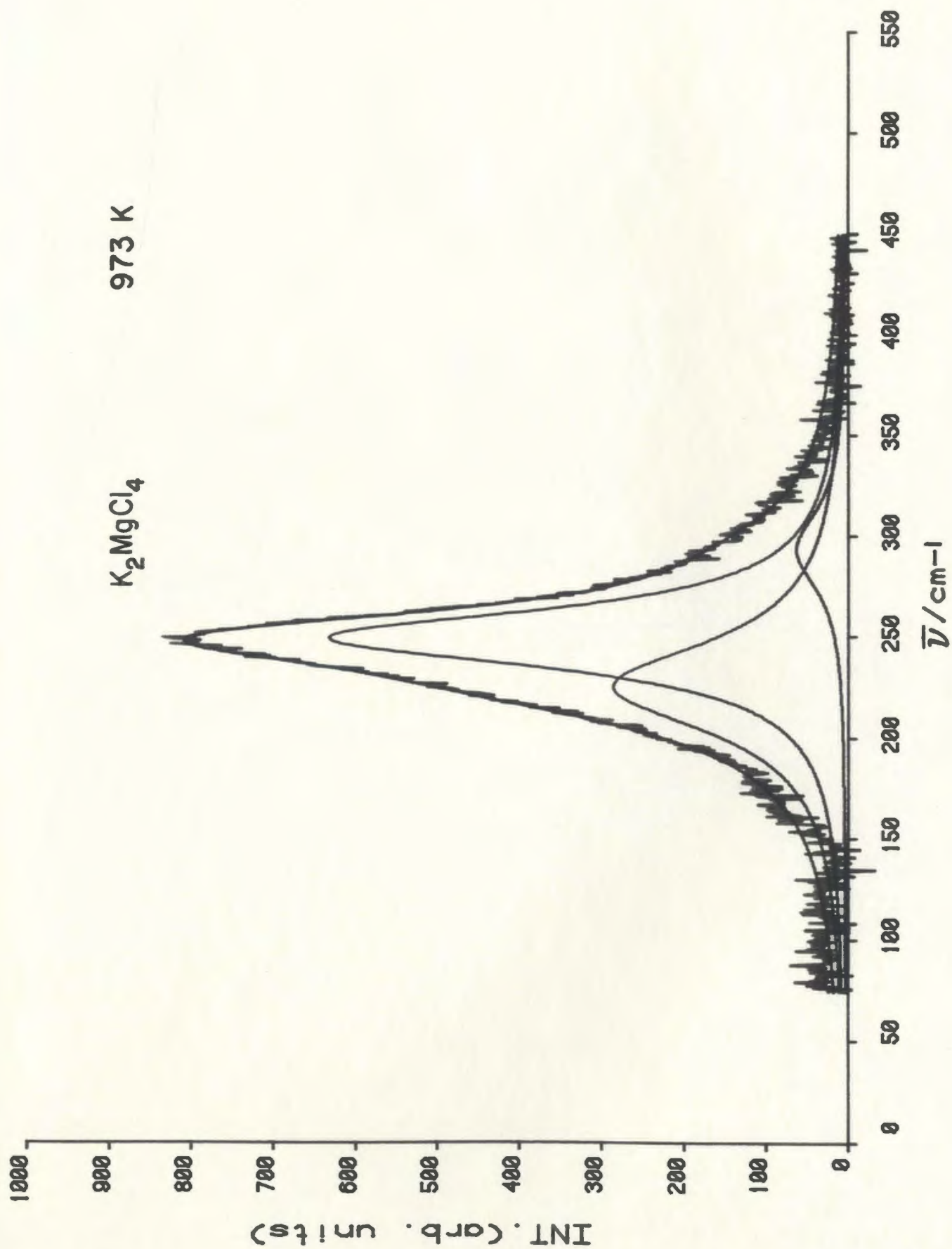
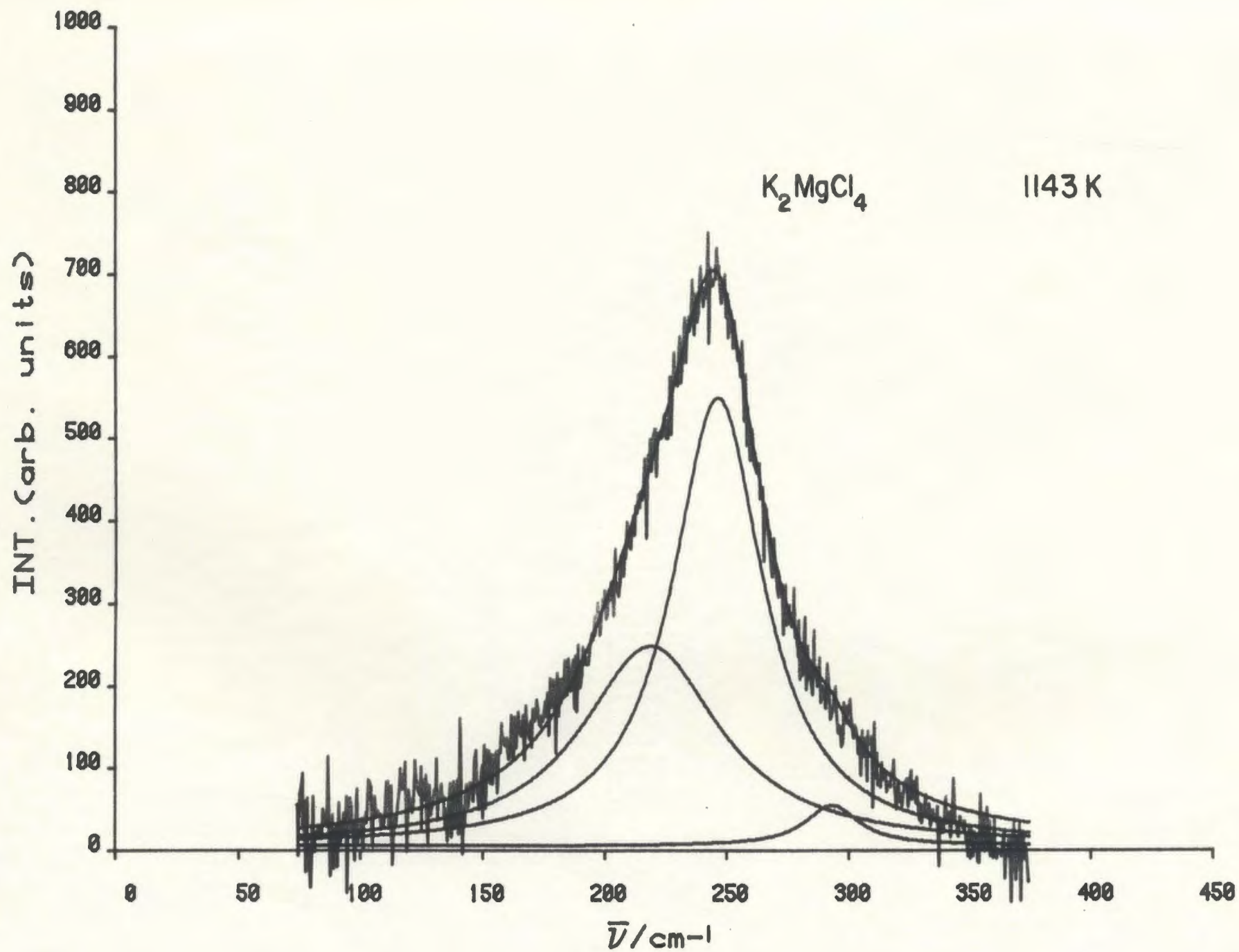




Figure 84. Isotropic Raman spectra of molten  $\text{K}_2\text{MgCl}_4$  at 1143 K.  
The smooth line is the best-fit curve calculated as  
a sum of three Lorentzian functions.



#### 4.3.4 Comparison of Results for $\text{MgCl}_2$ and $\text{MnCl}_2$ systems

The Raman spectra of  $\text{MnCl}_2$  and  $\text{MnCl}_2\text{-ACl}$  melts indicated that the  $\text{MnCl}_4^{2-}$  species is the predominant species in melts of composition  $\text{MnCl}_2 \cdot n\text{ACl}$  ( $n \leq 2$ ), and melts of higher  $\text{MnCl}_2$  concentration most probably contain a rapid equilibrium between  $\text{MnCl}_4^{2-}$  and  $\text{Mn}_2\text{Cl}_7^{3-}$  and perhaps octahedral  $\text{MnCl}_6^{4-}$ . The coordination number is not well defined because the exchange lifetime for  $\text{Cl}^-$  in the  $\text{Mn}^{2+}$  coordination sphere is short and near the Raman detection limit. Only one band was observed due to the Mn-Cl stretching vibration averaged over all coordinations and broadened by the wide range of environmental arrangements and  $\text{Cl}^-$  exchange. The Raman results of  $\text{MgCl}_2$ ,  $\text{MgCl}_2\text{-CsCl}$  and  $\text{MgCl}_2\text{-KCl}$  melts indicate that the  $\text{MgCl}_4^{2-}$  ions are the predominant species in these melts. However, by increasing the concentration of  $\text{MgCl}_2$  the polynuclear species  $\text{Mg}_2\text{Cl}_7^{3-}$  is formed, and for a further increment of  $\text{MgCl}_2$  concentration a third species is detected and attributed to polynuclear  $\text{Mg}_2\text{Cl}_n^{4-n}$  species. In contrast to the  $\text{MnCl}_2$  system, the  $\text{MgCl}_2$  system contains species that are long-lived enough to distinguish spectroscopically.



#### 4.4 Visible Spectra of $\text{MnCl}_2 \cdot n\text{H}_2\text{O}$

The ground state<sup>78,79</sup> of  $\text{Mn}^{+2}$  ion has five unpaired d-electrons, so the multiplicity for the ground level  $2S + 1 = 2(\frac{5}{2}) + 1 = 6$  i.e. the ground state has spin sextuplet. The ground state of the free ion has no spacial degeneracy and it has the symbol  ${}^6S$ . Besides the ground state  ${}^6S$ ,  $\text{Mn}^{+2}$  ion has excited states, four quartet terms  ${}^4G$ ,  ${}^4P$ ,  ${}^4D$  and  ${}^4F$ , and a number of doublet terms. The doublet states are of high energy and transition to them from the sextuplet ground state can only be observed at very low temperature in very thick crystals. The terms of the free ion and the splitting terms for  $\text{Mn}^{+2}$  ion in octahedral field are shown (Table 29). These terms can be applied in a tetrahedral field if the g subscripts are dropped, because  $T_d$  symmetry has no center of inversion and so the electronic states have no longer g or u character<sup>86</sup>.

The spectrum of  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  has been measured by Heidt et. al.<sup>80</sup>, Jorgensen<sup>81</sup> and Orgel<sup>82</sup>. The characteristic band positions and assignments of Heidt et. al. are shown in Table 30. Compounds which contain the octahedrally coordinated  $\text{Mn}^{2+}$  exhibit a characteristic pale red color as a consequence of weak absorption in the 17000 to 20000  $\text{cm}^{-1}$  region. Studies<sup>83-85</sup> of the absorption spectra of solid manganese halide crystals indicated the presence of octahedrally coordinated  $\text{Mn}^{2+}$ . The diffuse reflectance spectrum of  $\text{MnCl}_2$  has been reported by Clark<sup>83</sup> and assignments were similar to those proposed by Stout<sup>84,85</sup> for manganese halides.

The absorption spectra of tetrahalogenomanganate (II) salts of onium cations have been studied<sup>86</sup> in nonaqueous polar solvents. It was noted that when these salts dissolved in polar solvents, a slightly yellow color was observed which is due to the anion  $[\text{MnX}_4]^{2-}$ . The

Table 29. Splitting of the sextet and quartet terms of a  $d^5$  ion in octahedral field.

$6S$	$6A_{1g}$			
$4P$	$4T_{1g}$			
$4D$	$4E_g$	$4T_{2g}$		
$4F$	$4A_{2g}$	$4T_{1g}$	$4T_{2g}$	
$4G$	$4A_{1g}$	$4E_g$	$4T_{1g}$	$4T_{2g}$

Table 30. Absorption spectrum of  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ .

Band positions ( $\text{cm}^{-1}$ )	Assignments
18870	${}^6\text{A}_{1g}({}^6\text{S}) \rightarrow {}^4\text{T}_{1g}({}^4\text{G})$
23120	$\rightarrow {}^4\text{T}_{2g}({}^4\text{G})$
24960 } 25275 }	$\rightarrow {}^4\text{E}_g, {}^4\text{A}_{1g}({}^4\text{G})$
27980	$\rightarrow {}^4\text{T}_{2g}({}^4\text{D})$
29750	$\rightarrow {}^4\text{E}_g({}^4\text{D})$
32960	$\rightarrow {}^4\text{T}_{1g}({}^4\text{P})$
40810	$\rightarrow {}^4\text{A}_{2g}({}^4\text{F})$



observed spectra of the solutions were identical in all solvents and independent of the cation and similar to the reflexion spectra of the solid salts. Three distinct absorption regions were observed in the range 20000 to 38000  $\text{cm}^{-1}$ , where ten transitions are expected.

Tetrahedral coordination of  $\text{Mn}^{2+}$  ion was proposed.

The absorption spectra<sup>87</sup> of tetrahalomanganate (II) ions  $[\text{MnX}_4]^{2-}$ ,  $\text{X} = \text{Cl}, \text{Br}, \text{I}$  have been studied in the solid state and in various solvents at 25°C. It was reported that the tetrahedral manganese (II) complex has a pale green, yellow or yellow-green color, and the larger crystals have a marked color while the very fine powders often appear practically colorless. Three absorption patterns were observed in the spectra of  $[\text{MnBr}_4]^{2-}$  ion in the region 20000 to 38000  $\text{cm}^{-1}$ . Three absorption bands were observed in the range 20000 to 25000  $\text{cm}^{-1}$  and attributed to transitions to the states originating from the  $^4\text{G}$  term of the free ion. A group of three absorptions was found in the range 25000 to 28000  $\text{cm}^{-1}$  arising from the  $^4\text{D}$  and  $^4\text{P}$  terms. A third set of three bands was expected in the region 36000 to 38000  $\text{cm}^{-1}$  due to transitions to the states arising from the  $^4\text{F}$  term, but these transitions were less easily observed than the two previous patterns because they appear in a region where solvent absorption and absorption due to some organic groups of the cation. The peak positions and assignments for  $[\text{MnCl}_4]^{2-}$  and  $[\text{MnBr}_4]^{2-}$  are shown in Table 31.

The absorption spectra of  $\text{MnCl}_2$  in  $\text{LiCl-KCl}$  eutectic at 436°C and  $\text{MnBr}_2$  in  $\text{LiBr-KBr}$  eutectic at 457°C have been investigated<sup>88</sup>. Two peaks were observed in both spectra around 360 millimicrons (27777  $\text{cm}^{-1}$ ) and 440 millimicrons (22727  $\text{cm}^{-1}$ ). It was concluded that  $\text{Mn(II)}$  ion in both the chloride and bromide melts is tetrahedrally coordinated. A

Table 31. Absorption spectra of  $[\text{MnBr}_4]^{2-}$  and  $[\text{MnCl}_4]^{2-}$ .

Band positions ( $\text{cm}^{-1}$ )		Assignments
$[\text{MnBr}_4]^{2-}$	$[\text{MnCl}_4]^{2-}$	
21350	21200	${}^6\text{A}_1({}^6\text{S}) \rightarrow {}^4\text{T}_1({}^4\text{G})$
22180	22400	$\rightarrow {}^4\text{T}_2({}^4\text{G})$
23000	23200	$\rightarrow {}^4\text{E}, {}^4\text{A}_1({}^4\text{G})$
25900	26300	$\rightarrow {}^4\text{T}_2({}^4\text{D})$
26750	27100	$\rightarrow {}^4\text{E}({}^4\text{D})$
27700	27900	$\rightarrow {}^4\text{T}_1({}^4\text{P})$
36150	38000	$\rightarrow {}^4\text{A}_2({}^4\text{F})$
36150		$\rightarrow {}^4\text{T}_1({}^4\text{F})$
37400		$\rightarrow {}^4\text{T}_2({}^4\text{F})$



further investigation<sup>89</sup> of the absorption spectra of  $\text{Mn}^{2+}$  ion in LiCl-KCl eutectic at 400 and 1000°C was done by Gruen and McBeth. The spectra were characterized by two absorption bands at  $\sim 22000$  and  $28000 \text{ cm}^{-1}$ , and attributed to transitions from the  $^6\text{S}$  ground state to upper  $^4\text{G}$ ,  $^4\text{P}$  and  $^4\text{D}$  states. The spectra were in good agreement with the previous work<sup>88</sup>. The results favoured the tetrahedral  $\text{MnCl}_4^{2-}$  species.

The optical spectra of  $[\text{MnX}_4]^{2-}$ ,  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ , were studied<sup>90</sup> at  $160^\circ\text{C}$  in the molten state for low melting organic salts. The spectra were similar to the spectra obtained at room temperature by previous authors<sup>86,87</sup>. The results indicated that the tetrahedral  $\text{Mn}^{2+}$  ion persisted into the fused salts. Islam<sup>91</sup> investigated the optical spectra of  $\text{MnBr}_2$  in molten tetra-n-Butyl phosphonium bromide at  $112^\circ\text{C}$ . The solution had a yellowish-green color. The spectra showed two sets of weak resolved peaks in the visible region between  $18870$  and  $28990 \text{ cm}^{-1}$  and assigned to  $^6\text{S} \rightarrow ^4\text{G}$ , and  $^6\text{S} \rightarrow ^4\text{P} + ^4\text{D}$  transitions. A third band was observed in the ultraviolet region and attributed to  $^6\text{S} \rightarrow ^4\text{F}$  transitions. It was suggested that the manganese (II) in molten tetra-n-Butyl phosphonium bromide forms a tetrahedral complex  $\text{MnBr}_4^{2-}$ .

The absorption spectra of  $\text{MnCl}_2\text{-AlCl}_3$  and  $\text{MnCl}_2\text{-CsCl}$  mixtures have been studied<sup>23</sup>. The spectra of  $\text{MnCl}_2$  with CsCl in the concentration range  $0 < X_{\text{MnCl}_2} \leq 0.33$  were less structured, but the Raman data indicated that the tetrahedral  $\text{MnCl}_4^{2-}$  was the dominate species. However, the spectra of  $\text{Mn}^{+2}$  in  $\text{MnCl}_2\text{-AlCl}_3$  melts,  $X_{\text{MnCl}_2} \leq 0.30$ , were attributed to octahedral coordination of  $\text{Mn}^{+2}$  ion.

The diffuse reflectance spectra<sup>92</sup> of a number of Manganese (II) compounds in which the metal is surrounded by octahedral and tetrahedral arrangements of halogen atoms have been studied. The compounds included



$\text{MnX}_2$ ,  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ,  $(\text{MeNH}_3)_2\text{MnCl}_4$ ,  $\alpha\text{-Cs}_2\text{MnCl}_4$ ,  $\text{K}_4\text{MnCl}_6$ ,  $\text{KMnCl}_3$ ,  $\text{Me}_4\text{NMnCl}_3$  and  $\text{Me}_4\text{NMnBr}_3$ . Also the spectrum of single crystal  $\text{MnCl}_2$  has been investigated<sup>93</sup> at 77°K. Band assignments for  $\text{MnCl}_2$  are shown in Table 32.

The optical spectra<sup>94,95</sup> of  $\text{Mn}^{2+}$  ions in NaCl and KCl single crystals using impurity concentration in the range 0.1 to 15 mole % have been studied at room temperature and at 77°K. The formation of  $\text{K}_4\text{MnCl}_6$  and  $\text{NaMnCl}_3$  complexes was thought to be probable at high concentrations, but direct evidence was not presented. Recently<sup>96,97,98</sup> the optical spectra of  $\text{Mn}^{2+}$  ions in the Suzuki-phase ( $6\text{NaCl}:\text{MnCl}_2$ ) have been studied in NaCl. The results indicated that an intense band at 231 nm is characteristic of the Suzuki phase.

#### 4.4.1 Solid state

##### (i) $\text{Cs}_2\text{MnCl}_4$ and $\text{Cs}_3\text{MnCl}_5$

The visible spectra of  $\text{Cs}_2\text{MnCl}_4$  and  $\text{Cs}_3\text{MnCl}_5$  at room temperature and at 681 K are shown in figures 85,86,87 and 88 respectively. These two compounds exhibit greenish-yellow color at room temperature and at 681 K. The X-ray studies<sup>64,43</sup> indicated the presence of discrete  $\text{MnCl}_4^{2-}$  tetrahedral species and Raman studies strongly confirmed the X-ray results.

It has been reported<sup>92</sup> that the absorption spectra of  $\alpha\text{-Cs}_2\text{MnCl}_4$  is identical in appearance to the spectra of  $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4$  which is pink, and this implicitly suggest that the manganese has an octahedral environment. The Raman results indicate that the red low temperature form of this solid and referred to as  $\alpha\text{-Cs}_2\text{MnCl}_4$  is really a hydrated solid  $\text{Cs}_2\text{MnCl}_4 \cdot 0.16\text{H}_2\text{O}$ . The so called high temperature form referred

Table 32. Electronic spectra of  $\text{MnCl}_2$ .

Band positions ( $\text{cm}^{-1}$ )		Assignments
$\text{MnCl}_2^{92}$	$\text{MnCl}_2^{93}$	
18900	18500	${}^6\text{A}_1({}^6\text{S}) \rightarrow {}^4\text{T}_1({}^4\text{G})$
22220	22000	$\rightarrow {}^4\text{T}_2({}^4\text{G})$
23870	23574 } 23800 }	$\rightarrow {}^4\text{A}_1, {}^4\text{E}({}^4\text{G})$
27030	27000	$\rightarrow {}^4\text{T}_2({}^4\text{D})$
28250	28066	$\rightarrow {}^4\text{E}({}^4\text{D})$
30490	30500	$\rightarrow {}^4\text{T}_1({}^4\text{P})$
	38400	$\rightarrow {}^4\text{A}_2, {}^4\text{T}_1({}^4\text{F})$
	40700	$\rightarrow {}^4\text{T}_2({}^4\text{F})$



to as  $\beta\text{-Cs}_2\text{MnCl}_4$  is the true anhydrous form and has a greenish yellow color.

One absorption pattern was observed at room temperature in both  $\text{Cs}_2\text{MnCl}_4$  and  $\text{Cs}_3\text{MnCl}_5$ . The observed peaks are close to the first three bands observed in the reflectance spectra<sup>87</sup> of  $[\text{MnCl}_4]^{2-}$  compounds. One peak is observed at 681 K for both samples, and slightly shifted to lower frequency on comparison to the counterpart observed at room temperature. Both compounds remained greenish-yellow until they melted and there was no evidence to suggest a phase transition. There is a weak peak observed at  $\sim 16000 \text{ cm}^{-1}$ , and it is most probably due to the presence of Manganese oxide<sup>99,100</sup> as a slight impurity in the sample. Band positions and assignments are shown in Table 33.

(ii)  $\text{MnCl}_2$ ,  $\text{NaMn}_4\text{Cl}_9$  and  $\text{Na}_2\text{Mn}_3\text{Cl}_8$

The visible spectra of  $\text{MnCl}_2$ ,  $\text{NaMn}_4\text{Cl}_9$  and  $\text{Na}_2\text{Mn}_3\text{Cl}_8$  at room temperature are shown in figures 89, 90 and 91 respectively. These compounds exhibit a pink color, and this suggests that they have octahedral environment<sup>71,68</sup>.

The peak observed in the spectrum of  $\text{MnCl}_2$  at  $\sim 18089 \text{ cm}^{-1}$  is due to  ${}^6\text{A}_{1g}({}^6\text{S}) \rightarrow {}^4\text{T}_{1g}({}^4\text{G})$  transition. A transition from the ground state  ${}^6\text{A}_{1g}({}^6\text{S})$  to the excited state  ${}^4\text{T}_{2g}({}^4\text{G})$  was reported<sup>83,84,92,93</sup> to appear around  $\sim 22000 \text{ cm}^{-1}$ , so this indicate that the shoulder observed at  $\sim 19826 \text{ cm}^{-1}$  is probably not real peak. The peak observed at  $\sim 16000 \text{ cm}^{-1}$  in the spectrum of  $\text{Na}_2\text{Mn}_3\text{Cl}_8$  is most probably attributed to Manganese oxide<sup>99,100</sup>. Band positions and assignments are shown in Table 34.



Figure 85. A. Upper spectrum is the projection lamp spectrum.  
Lower spectrum is the projection lamp plus  
sample spectrum.

B. The subtracted spectrum represents the visible  
spectrum of  $\text{Cs}_2\text{MnCl}_4$  at room temperature.

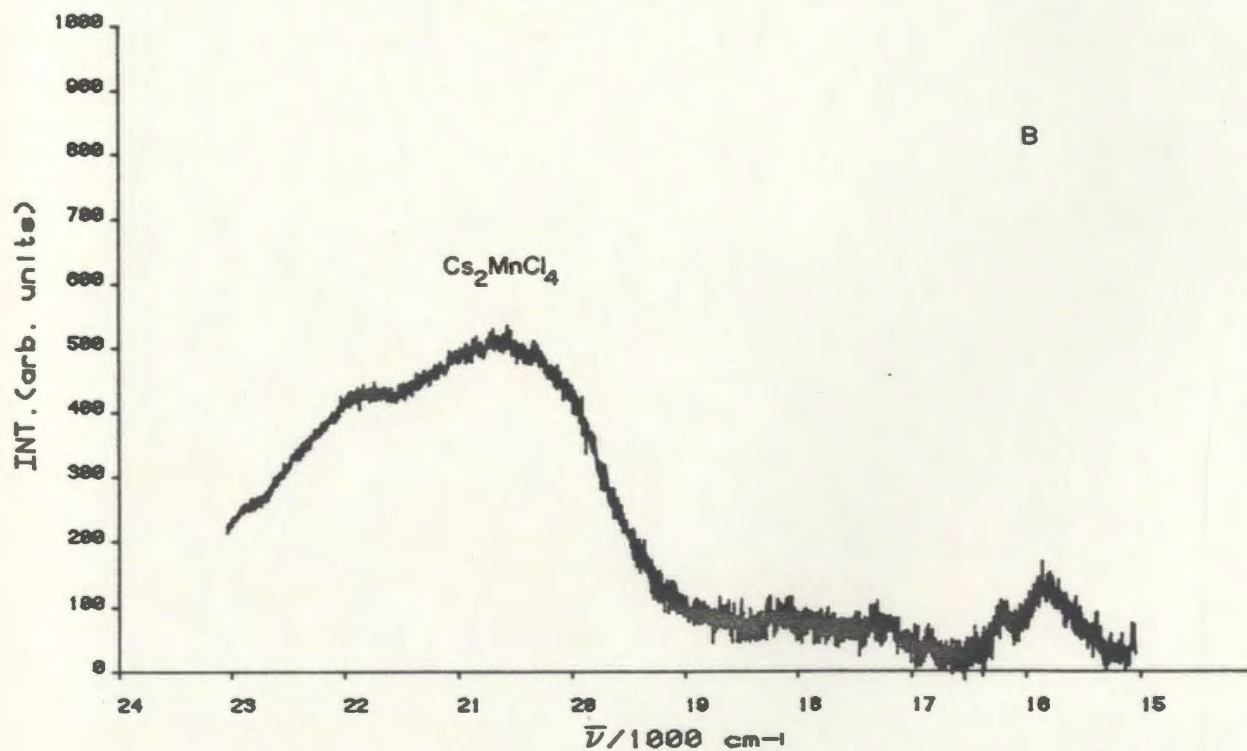
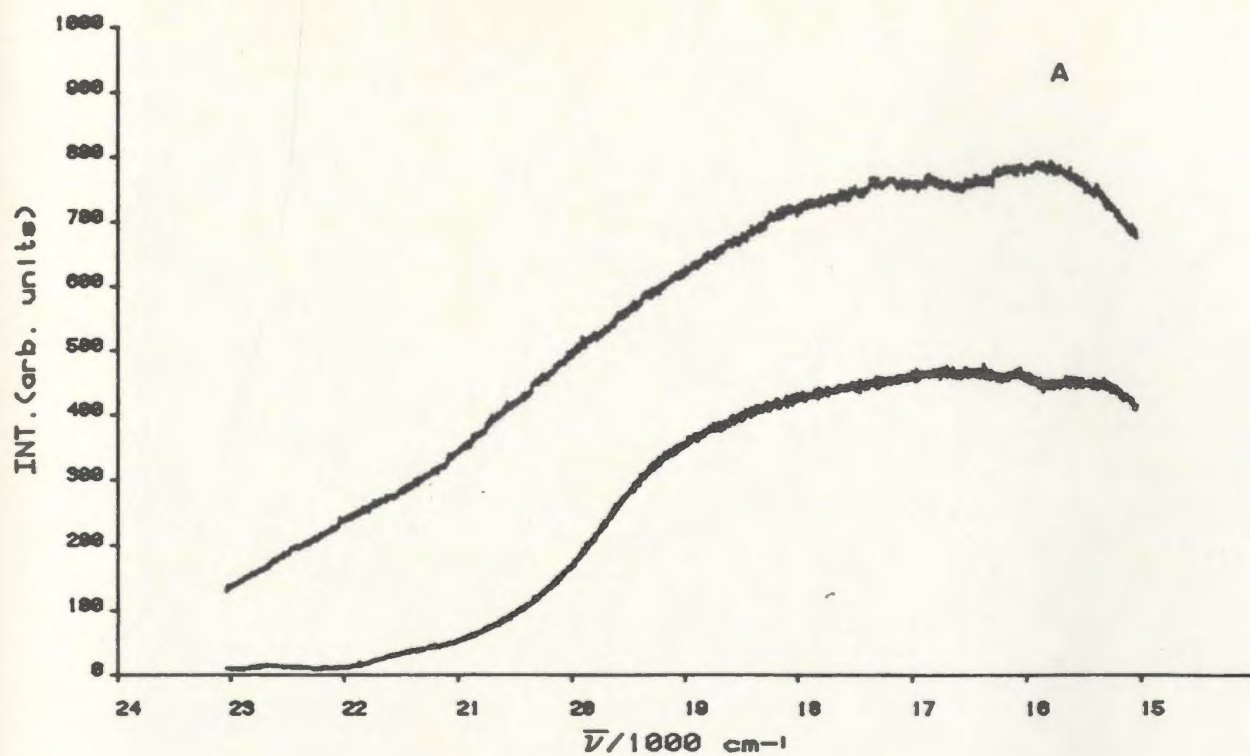


Figure 86. Visible spectrum of  $\text{Cs}_2\text{MnCl}_4$  at 681 K.



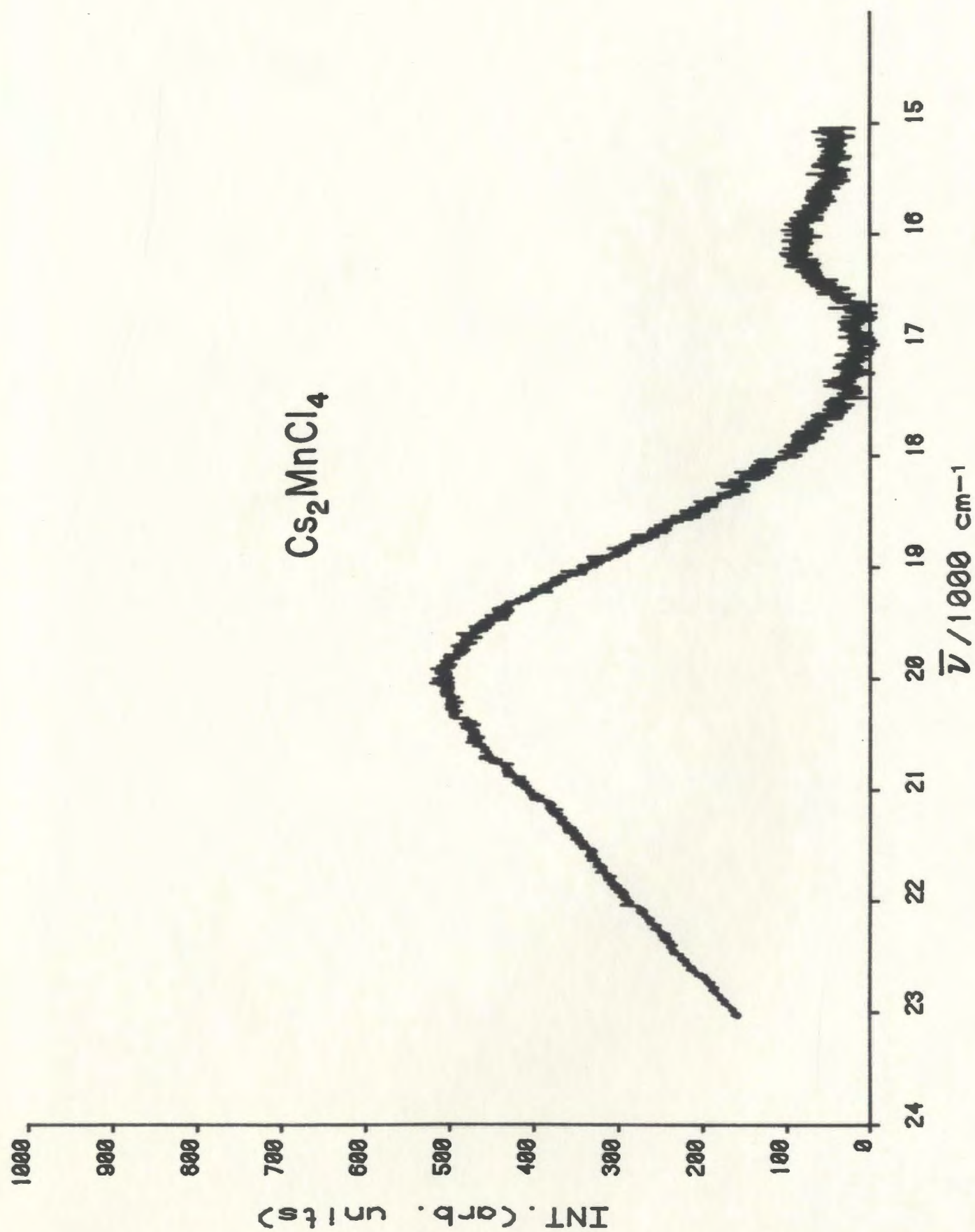


Figure 87. Visible spectrum of  $\text{Cs}_3\text{MnCl}_5$  at room temperature.

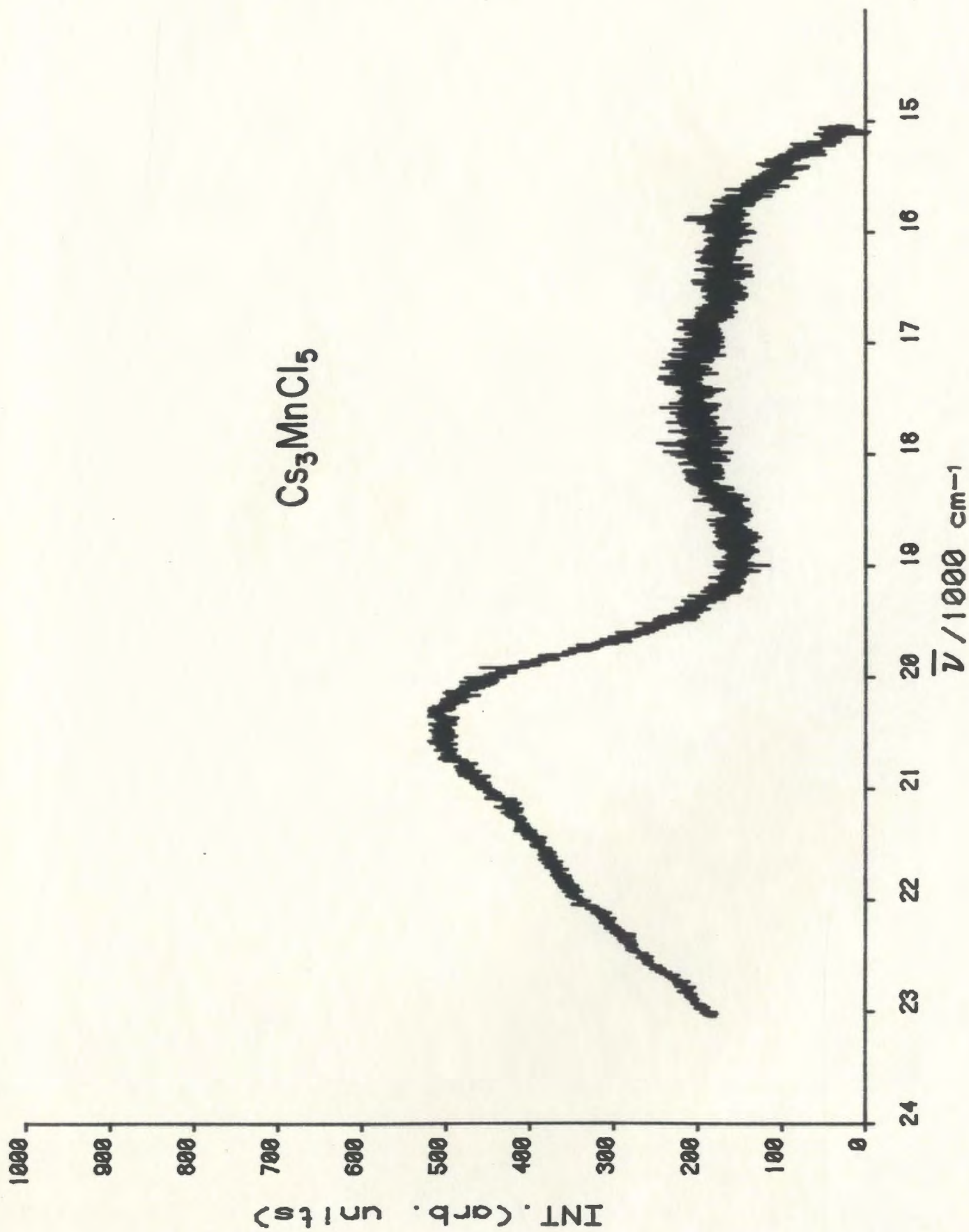
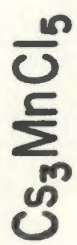




Figure 88. Visible spectrum of  $\text{Cs}_3\text{MnCl}_5$  at 681 K.

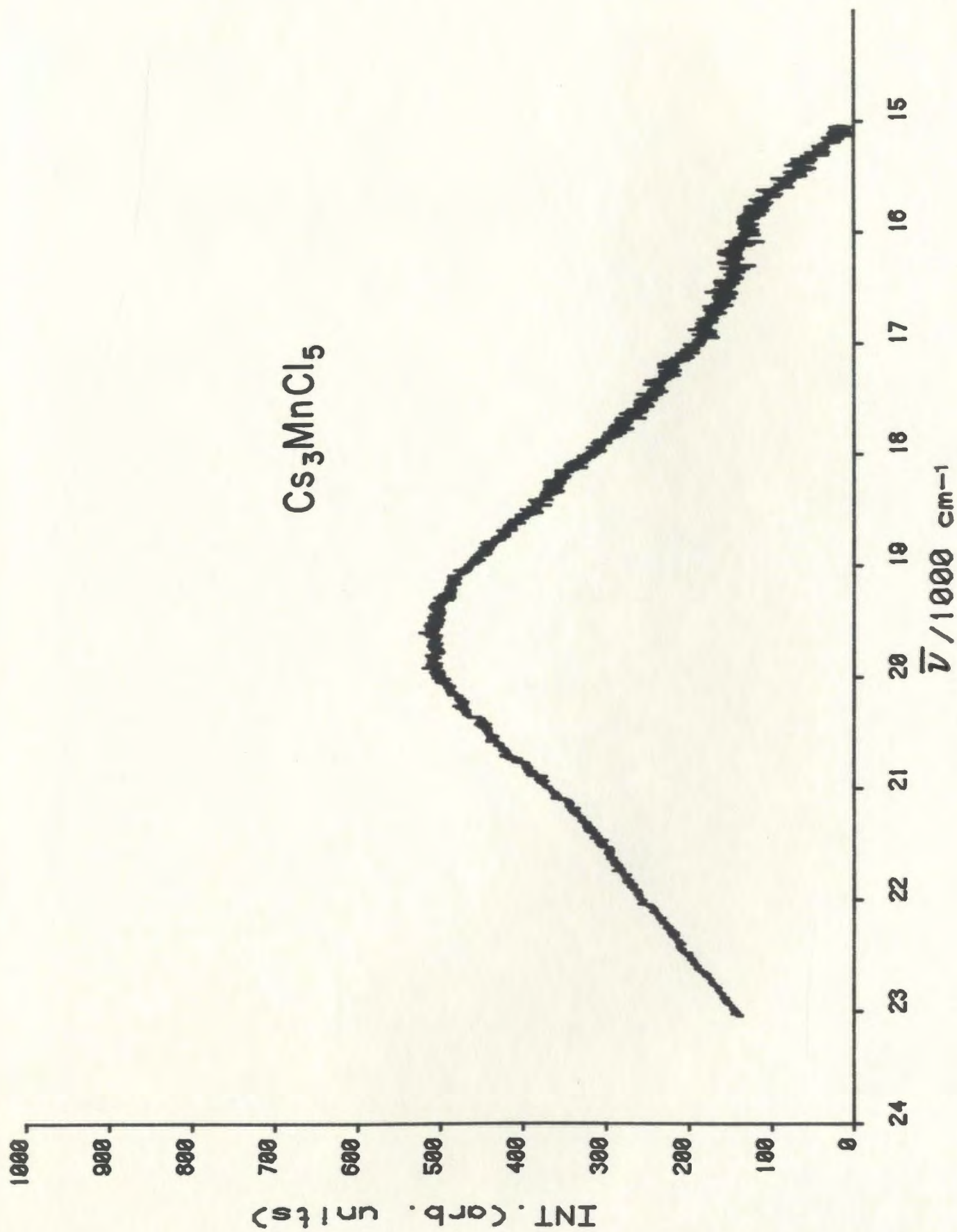


Table 33. Band positions in  $\text{cm}^{-1}$  and assignments for solid  $\text{Cs}_2\text{MnCl}_4$  and  $\text{Cs}_3\text{MnCl}_5$ .

Assignments	$\text{Cs}_2\text{MnCl}_4$ at Room Temp.	$\text{Cs}_2\text{MnCl}_4$ at 681 K	$\text{Cs}_3\text{MnCl}_5$ at Room Temp.	$\text{Cs}_3\text{MnCl}_5$ at 681 K	$[\text{MnCl}_4]^{2-}$ ions <sup>87</sup>
${}^6\text{A}_1({}^6\text{S}) \rightarrow {}^4\text{T}_1({}^4\text{G})$	20542	20042	20542	19742	21050
$\rightarrow {}^4\text{T}_2({}^4\text{G})$	21802		21802		22000
$\rightarrow {}^4\text{E}, {}^4\text{A}_1({}^4\text{G})$	22802		22802		23000



Figure 89. Visible spectrum of  $\text{MnCl}_2$  at room temperature.

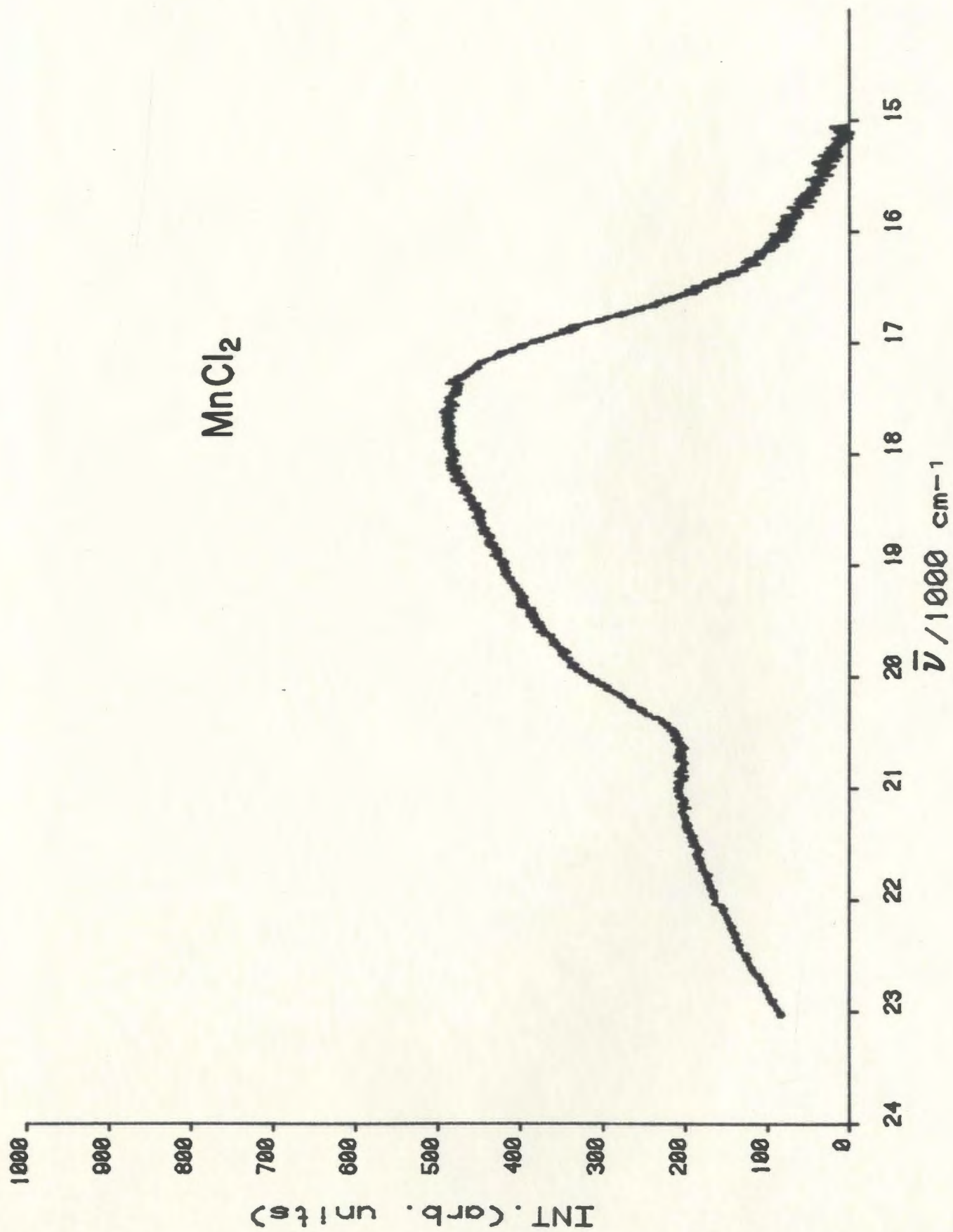


Figure 90. Visible spectrum of  $\text{NaMn}_4\text{Cl}_9$  at room temperature.



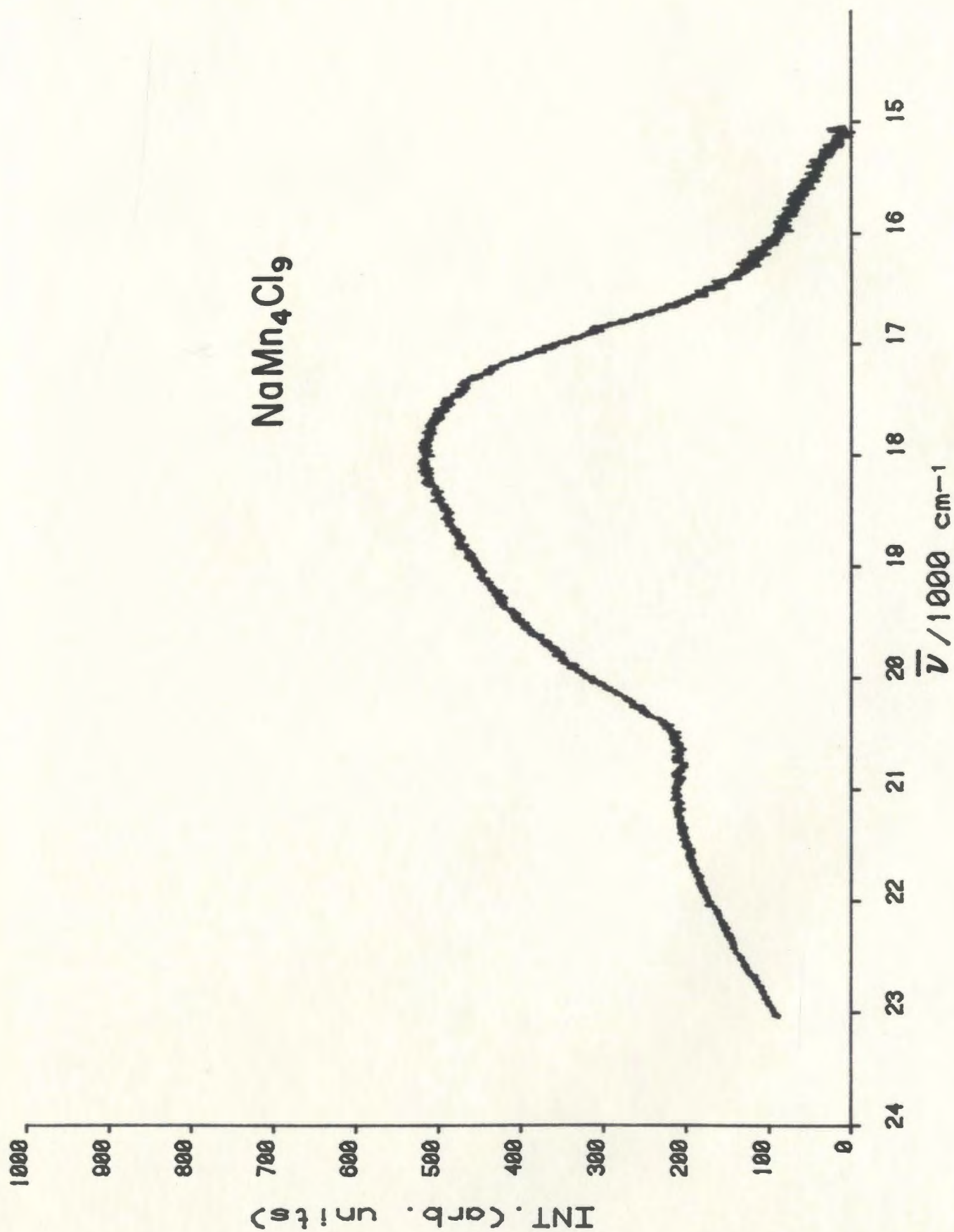


Figure 91. Visible spectrum of  $\text{Na}_2\text{Mn}_3\text{Cl}_8$  at room temperature.

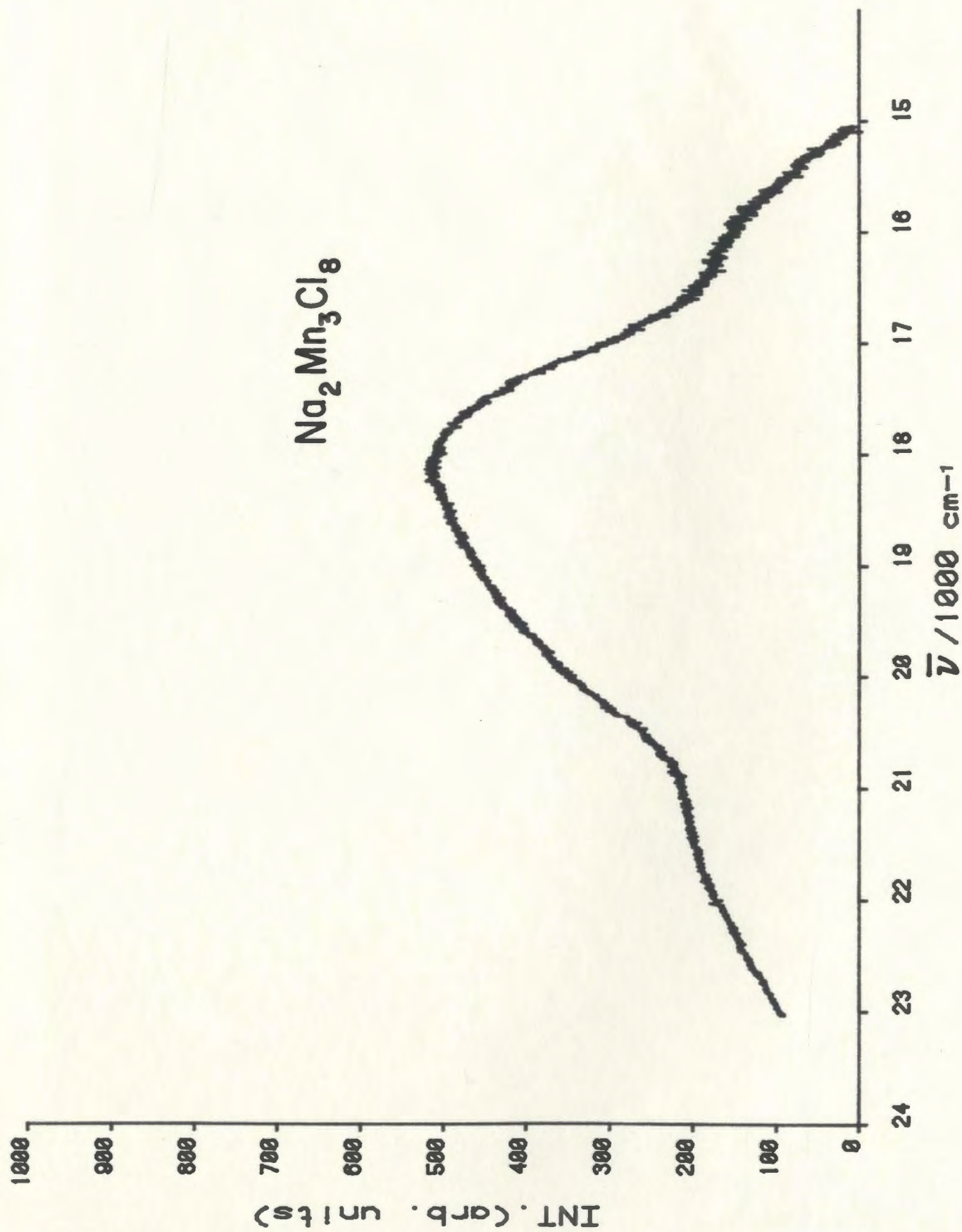
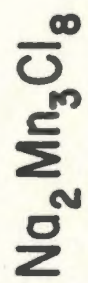




Table 34. Peak frequencies in  $\text{cm}^{-1}$  and assignments for solid  $\text{MnCl}_2$ ,  $\text{NaMn}_4\text{Cl}_9$  and  $\text{Na}_2\text{Mn}_3\text{Cl}_8$  at room temperature.

Assignments	$\text{MnCl}_2$	$\text{MnCl}_2^{83}$	$\text{NaMn}_4\text{Cl}_9$	$\text{Na}_2\text{Mn}_3\text{Cl}_8$
${}^6\text{A}_{1g}({}^6\text{S}) \rightarrow {}^4\text{T}_{1g}({}^4\text{G})$	18089	18650	18159	18259
$\rightarrow {}^4\text{T}_{2g}({}^4\text{G})$	21099	22100	21099	21099

(iii) CsMnCl<sub>3</sub> and CsMn<sub>4</sub>Cl<sub>9</sub>

The visible spectra of CsMnCl<sub>3</sub> and CsMn<sub>4</sub>Cl<sub>9</sub> at room temperature and at 681 K are shown in figures 92, 93, 94 and 95 respectively. These compounds are pink at room temperature and at 681 K. It was reported that the Mn<sup>2+</sup> ion has an octahedral environment in CsMnCl<sub>3</sub><sup>52</sup> and CsMn<sub>4</sub>Cl<sub>9</sub><sup>39</sup>. The shoulder observed at ~ 16000 cm<sup>-1</sup> in the spectrum of CsMn<sub>4</sub>Cl<sub>9</sub> at room temperature is probably due to Manganese oxide<sup>99,100</sup>. Band assignments are shown in Table 35.

(iv) RbMnCl<sub>3</sub>, Rb<sub>2</sub>MnCl<sub>4</sub> and Rb<sub>3</sub>Mn<sub>2</sub>Cl<sub>7</sub>

The visible spectra of RbMnCl<sub>3</sub>, Rb<sub>2</sub>MnCl<sub>4</sub>, and Rb<sub>3</sub>Mn<sub>2</sub>Cl<sub>7</sub> at room temperature are shown in figures 96, 97 and 98 respectively. RbMnCl<sub>3</sub> has an orange-slight red color, while Rb<sub>2</sub>MnCl<sub>4</sub> and Rb<sub>3</sub>Mn<sub>2</sub>Cl<sub>7</sub> exhibit bright orange color. So it is noted that the peak observed at ~ 18709 cm<sup>-1</sup> in RbMnCl<sub>3</sub> is slightly shifted to lower frequency in comparison to its counterpart observed in Rb<sub>2</sub>MnCl<sub>4</sub> and Rb<sub>3</sub>Mn<sub>2</sub>Cl<sub>7</sub>.

The X-ray study<sup>56</sup> of RbMnCl<sub>3</sub> indicated that the manganese has an octahedral environment. It was reported<sup>43</sup> that Rb<sub>2</sub>MnCl<sub>4</sub> is isomorphous with K<sub>2</sub>MgCl<sub>4</sub><sup>42</sup> in which the magnesium is octahedrally coordinated by Cl atoms. Seifert<sup>43</sup> reported that Rb<sub>3</sub>Mn<sub>2</sub>Cl<sub>7</sub> is isostructural with Sr<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub> which has a tetragonal structure<sup>61</sup> in which the titanium is surrounded by six oxygen atoms, so this implicitly indicates that the manganese is octahedrally coordinated by Cl atoms. Band positions in cm<sup>-1</sup> and assignments are shown in Table 36.

(v) KMnCl<sub>3</sub>, K<sub>4</sub>MnCl<sub>6</sub> and K<sub>3</sub>Mn<sub>2</sub>Cl<sub>7</sub>

The visible spectra of KMnCl<sub>3</sub>, K<sub>4</sub>MnCl<sub>6</sub> and K<sub>3</sub>Mn<sub>2</sub>Cl<sub>7</sub> at room

Figure 92. Visible spectrum of  $\text{CsMnCl}_3$  at room temperature.



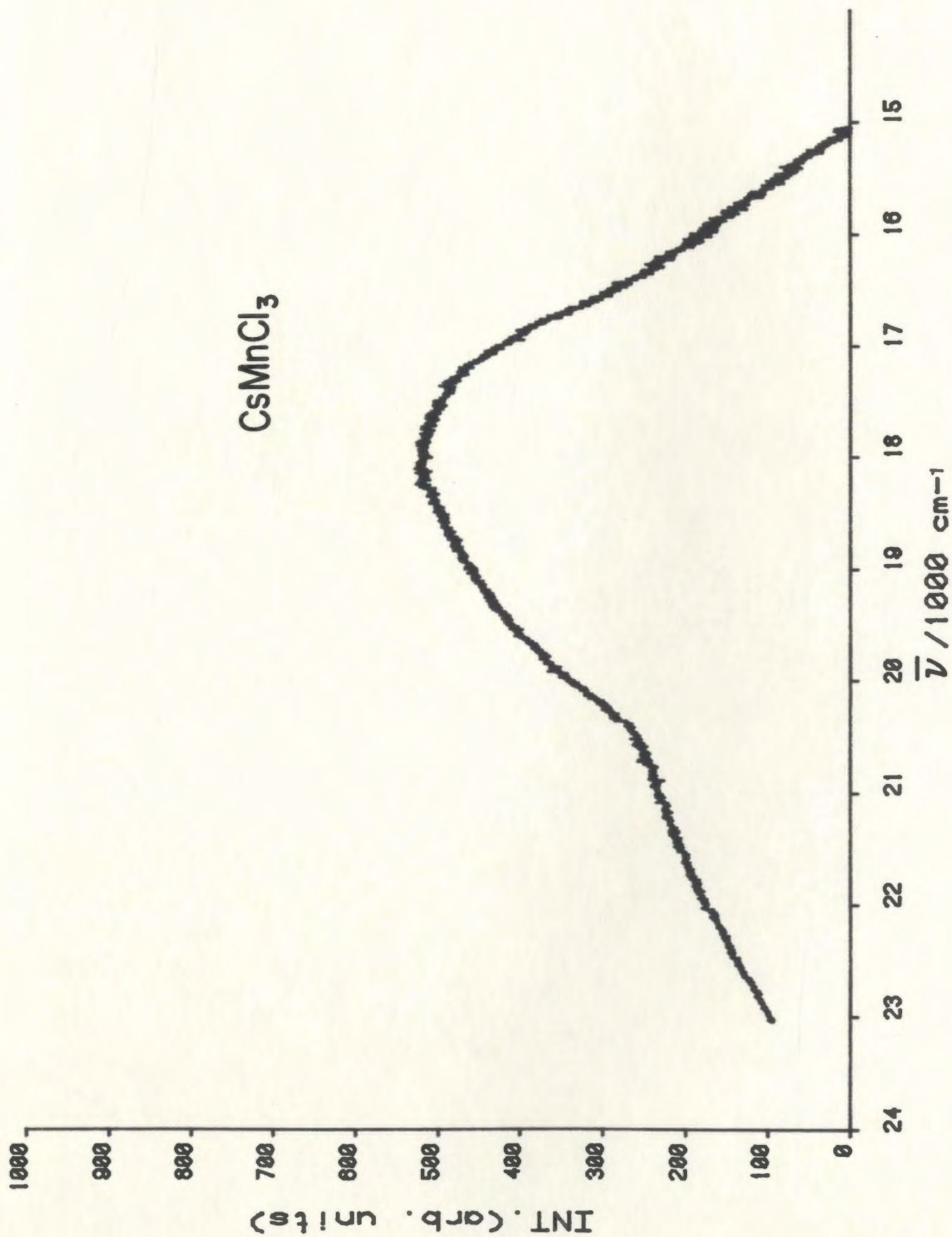


Figure 93. Visible spectrum of  $\text{CsMnCl}_3$  at 681 K.

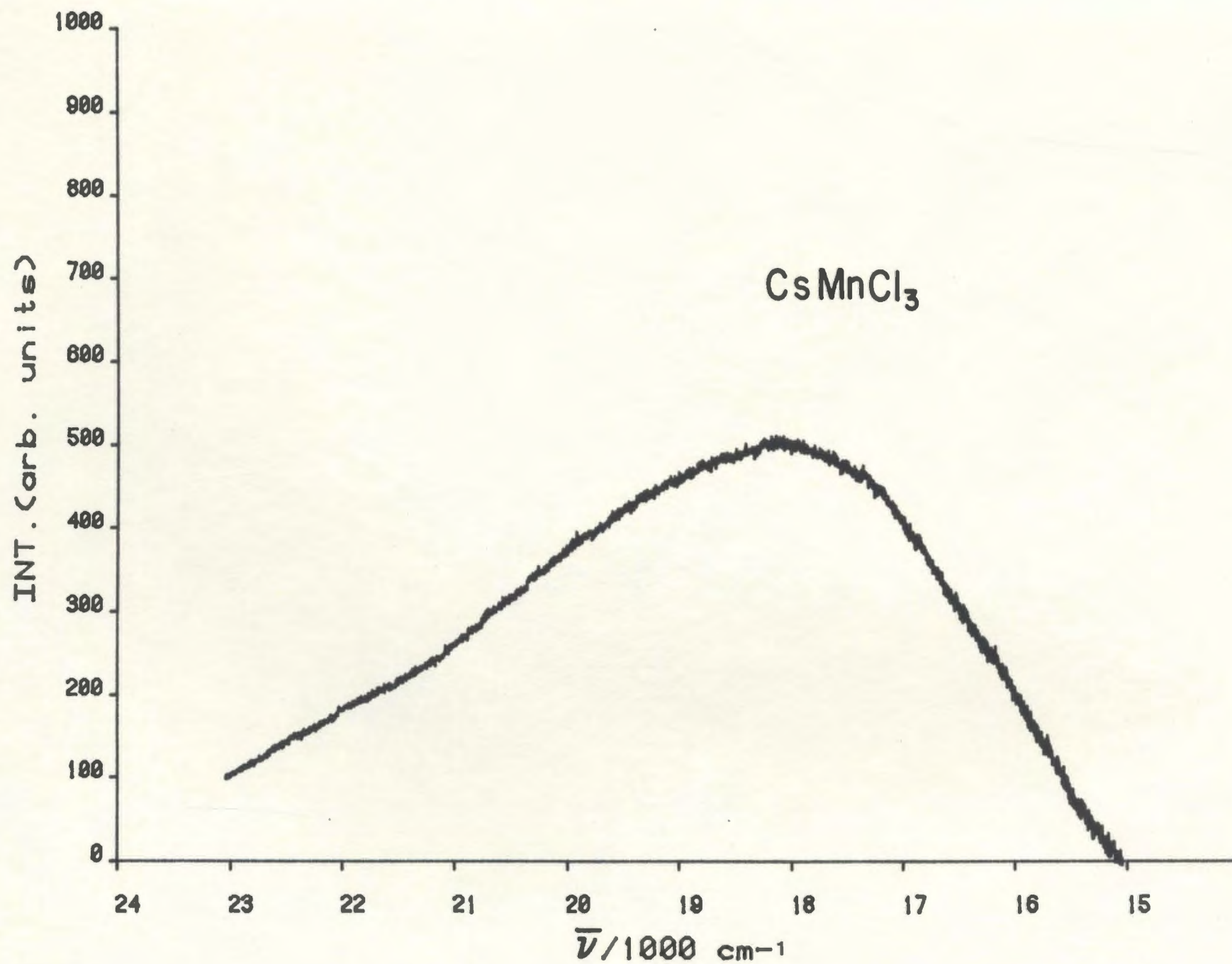




Figure 94. Visible spectrum of  $\text{CsMn}_4\text{Cl}_9$  at room temperature.

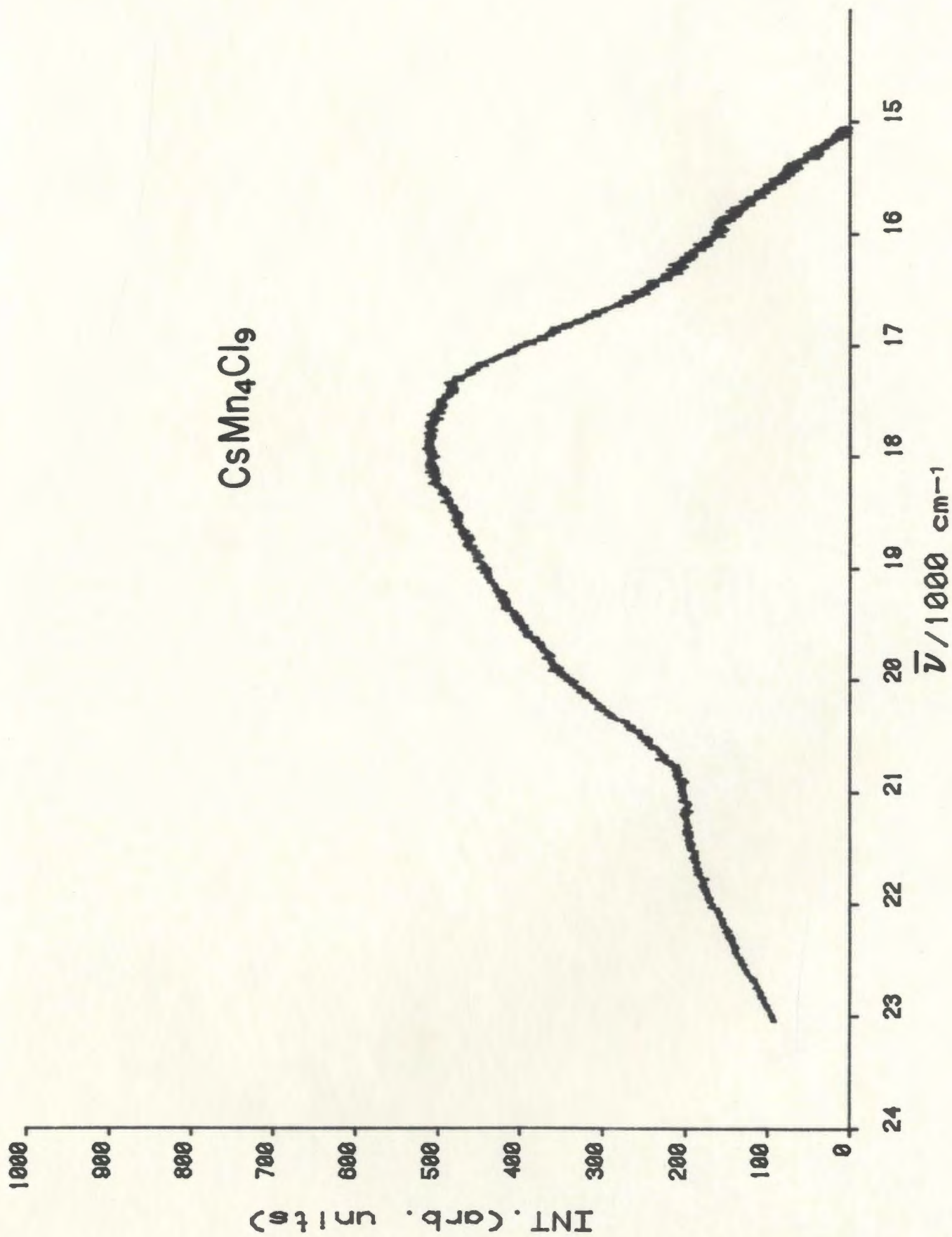


Figure 95. Visible spectrum of  $\text{CsMn}_4\text{Cl}_9$  at 681 K.



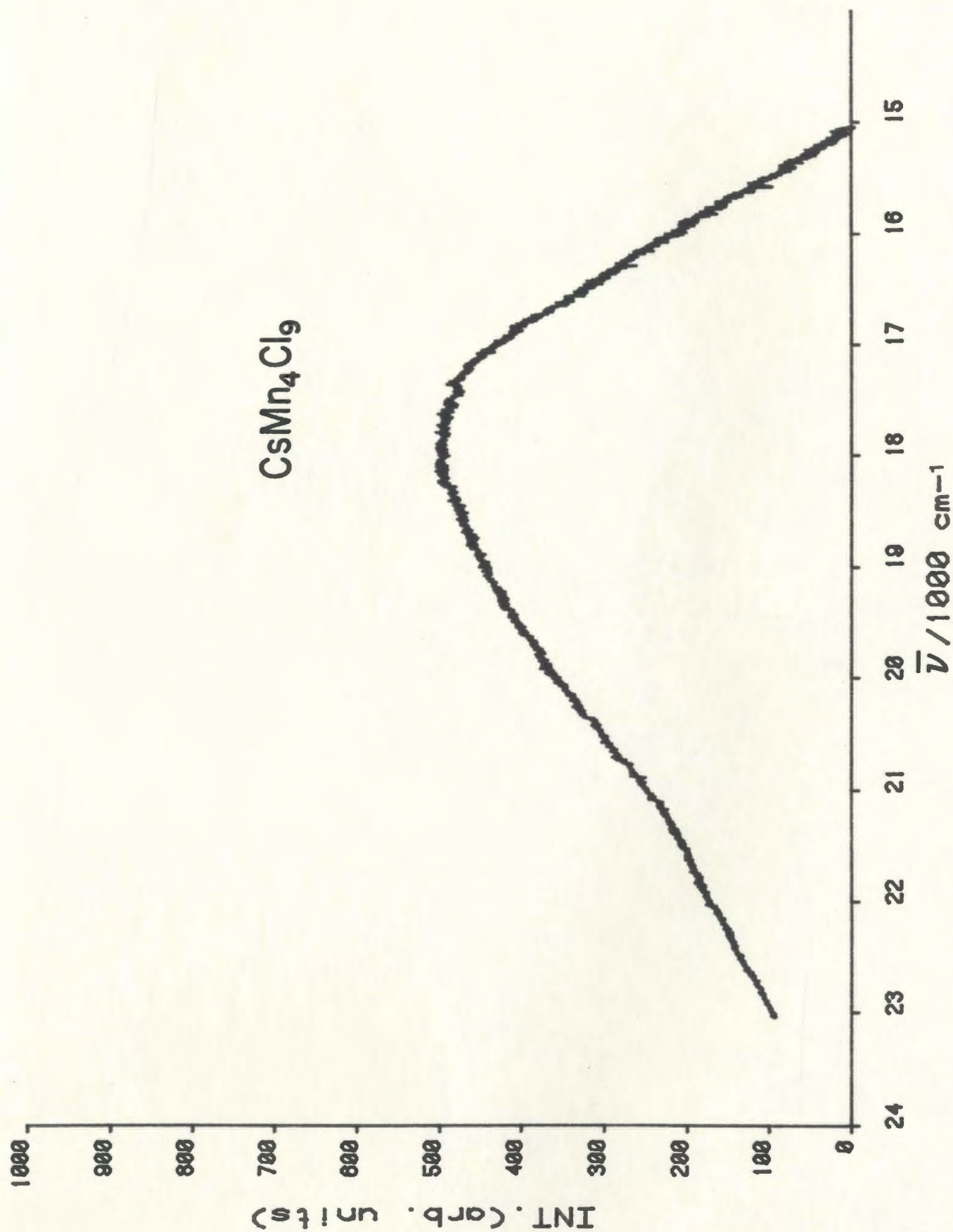


Table 35. Peak positions in  $\text{cm}^{-1}$  and assignments for solid  $\text{CsMnCl}_3$ ,  $\text{CsMn}_4\text{Cl}_9$  and  $(\text{CH}_3)_4\text{NMnCl}_3$ .

Assignments	$\text{CsMnCl}_3$ at Room Temp.	$\text{CsMnCl}_3$ at 681 K	$\text{CsMn}_4\text{Cl}_9$ at Room Temp.	$\text{CsMn}_4\text{Cl}_9$ at 681 K	$(\text{CH}_3)_4\text{NMnCl}_3$ <sup>92</sup>
${}^6\text{A}_{1g}({}^6\text{S}) \rightarrow {}^4\text{T}_{1g}({}^4\text{G})$	18042	18042	18042	18042	18840
$\rightarrow {}^4\text{T}_{2g}({}^4\text{G})$	21000		21099		22560

Figure 96. Visible spectrum of  $\text{RbMnCl}_3$  at room temperature.



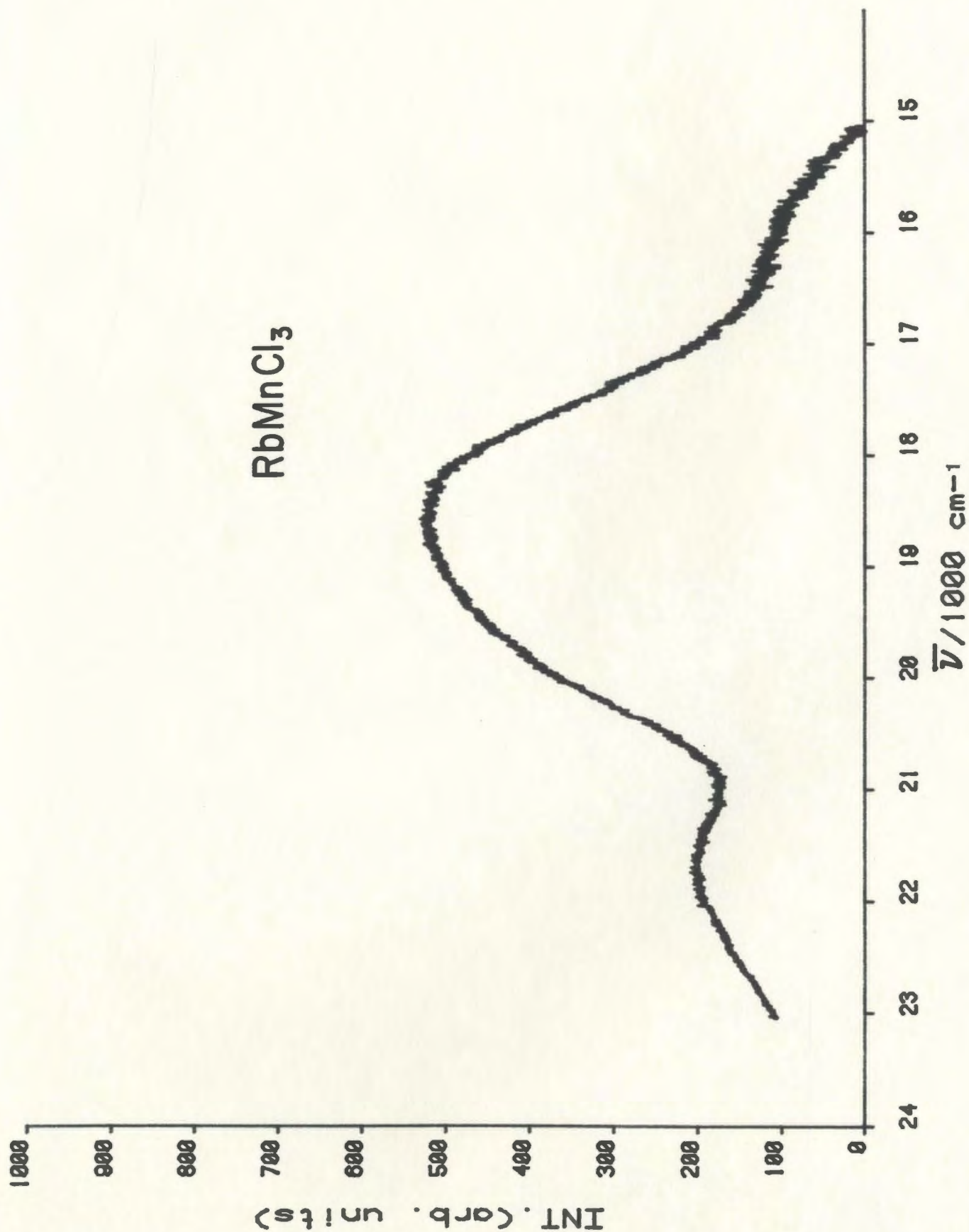


Figure 97. Visible spectrum of  $\text{Rb}_2\text{MnCl}_4$  at room temperature.

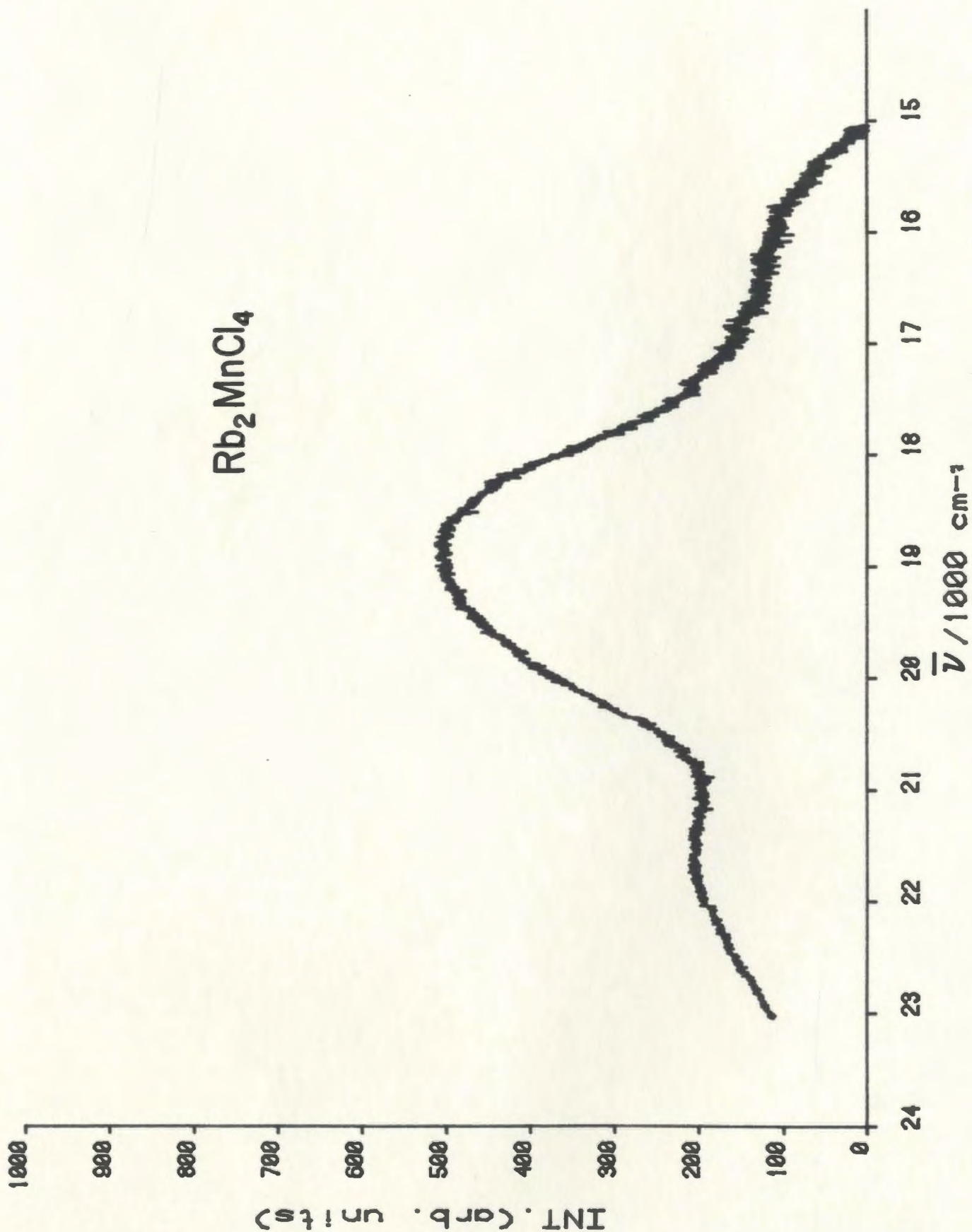




Figure 98. Visible spectrum of  $\text{Rb}_3\text{Mn}_2\text{Cl}_7$  at room temperature.

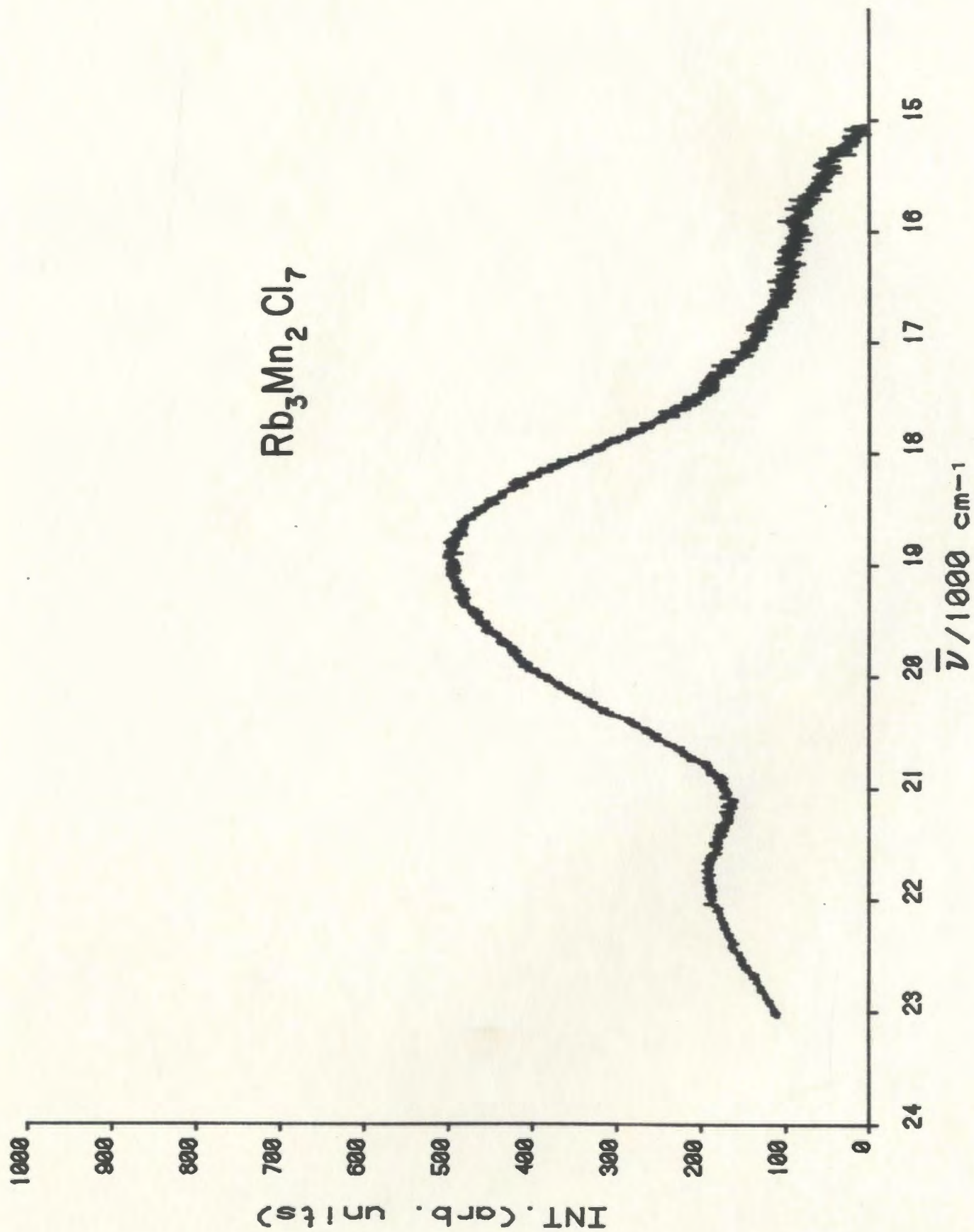


Table 36. Peak frequencies in  $\text{cm}^{-1}$  and assignments for solid  $\text{RbMnCl}_3$ ,  $\text{Rb}_2\text{MnCl}_4$  and  $\text{Rb}_3\text{Mn}_2\text{Cl}_7$  at room temperature.

Assignments	$\text{RbMnCl}_3$	$\text{Rb}_2\text{MnCl}_4$	$\text{Rb}_3\text{Mn}_2\text{Cl}_7$
${}^6\text{A}_{1g}({}^6\text{S}) \rightarrow {}^4\text{T}_{1g}({}^4\text{G})$	18709	18942	18942
$\rightarrow {}^4\text{T}_{2g}({}^4\text{G})$	21788	21788	21788



temperature are shown in figures 99, 100 and 101 respectively. These compounds exhibit orange color.

Seifert<sup>64</sup> reported that  $\text{Mn}^{2+}$  ions occupy octahedral holes in compounds of the formula  $\text{AMnX}_3$ , so the  $\text{Mn}^{2+}$  ions in  $\text{KMnCl}_3$  have an octahedral arrangement. Also<sup>64</sup> he suggested that compounds of the formula  $\text{A}_4\text{MnX}_6$  contain isolated  $\text{MnX}_6$  octahedra, so this indicate that the Mn atom in  $\text{K}_4\text{MnCl}_6$  is octahedrally coordinated by Cl atoms.  $\text{K}_3\text{Mn}_2\text{Cl}_7$ <sup>43</sup> is isostructural with  $\text{Rb}_3\text{Mn}_2\text{Cl}_7$ , in which the Mn atom has an octahedral environment.

The spectrum of  $\text{K}_4\text{MnCl}_6$  is similar in appearance to the reflectance spectrum reported by Foster and Gill<sup>92</sup>. The peaks observed in the reflectance spectrum<sup>92</sup> of  $\text{KMnCl}_3$  at  $\sim 19700$  and at  $\sim 22960$  were assigned to  ${}^6\text{S} \rightarrow {}^4\text{G}$  transitions, so the shoulder observed at  $\sim 20542 \text{ cm}^{-1}$  in the spectrum of  $\text{KMnCl}_3$  is probably not real peak. Assignments and peak positions in  $\text{cm}^{-1}$  are shown in Table 37.

(vi)  $\text{NaMnCl}_3$ ,  $\text{Na}_2\text{MnCl}_4$  and  $\text{Na}_6\text{MnCl}_8$

The visible spectra of  $\text{NaMnCl}_3$ ,  $\text{Na}_2\text{MnCl}_4$  and  $\text{Na}_6\text{MnCl}_8$  at room temperature are shown in figures 102, 103 and 104.  $\text{NaMnCl}_3$  and  $\text{Na}_2\text{MnCl}_4$  have an orange color while  $\text{Na}_6\text{MnCl}_8$  is colorless.

The manganese has an octahedral environment in  $\text{NaMnCl}_3$ <sup>65</sup> and  $\text{Na}_2\text{MnCl}_4$ <sup>67</sup>. It was reported<sup>68</sup> that the Mn in  $\text{Na}_6\text{MnCl}_8$  has an octahedral arrangement.

The peak observed at  $19256 \text{ cm}^{-1}$  in the spectrum of  $\text{Na}_6\text{MnCl}_8$  is close to its counterpart observed in the Suzuki phase spectrum<sup>96,97,98</sup>. Band assignments and frequency in  $\text{cm}^{-1}$  are shown in Table 38.

Figure 99. Visible spectrum of  $\text{KMnCl}_3$  at room temperature.

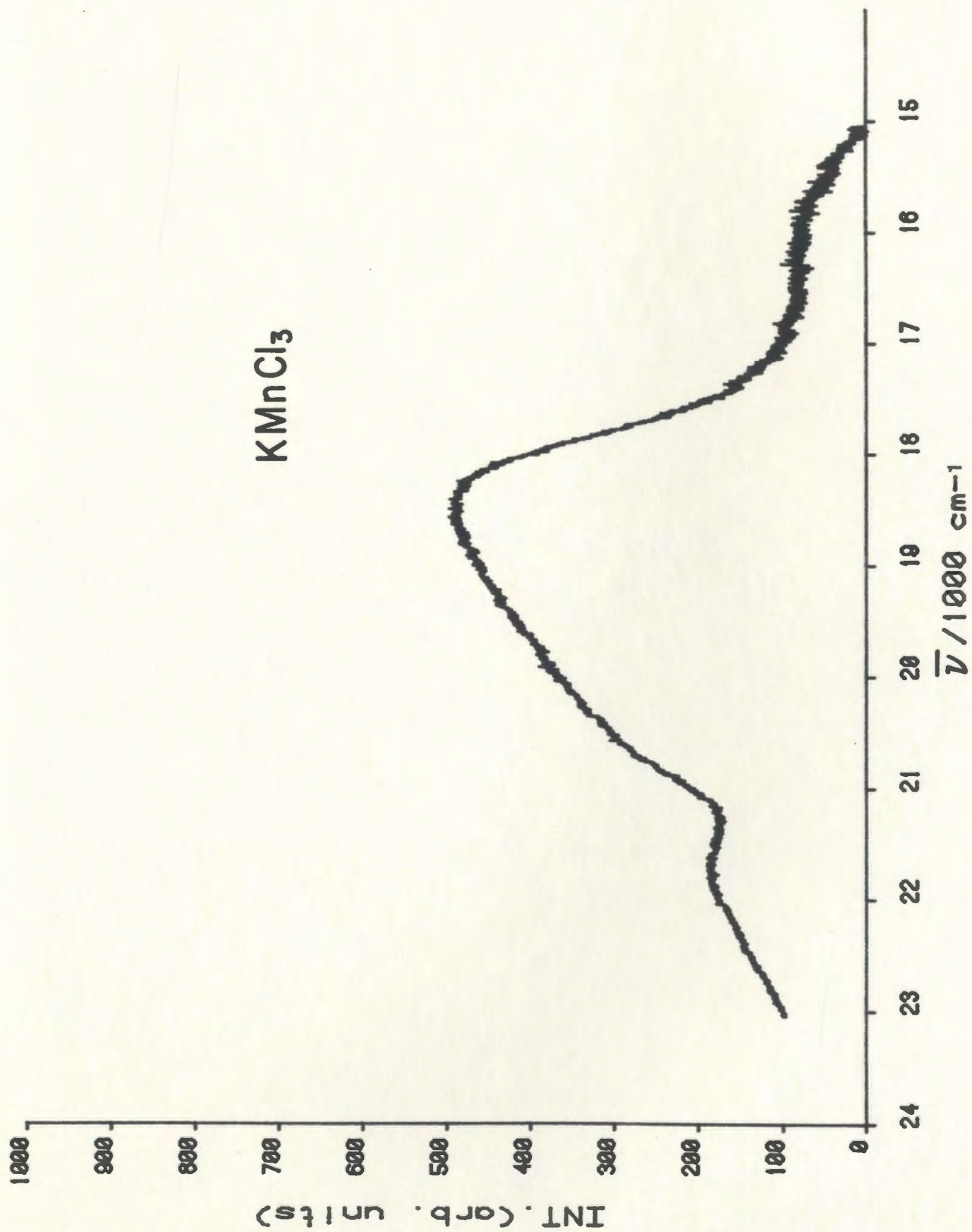




Figure 100. Visible spectrum of  $\text{K}_4\text{MnCl}_6$  at room temperature.

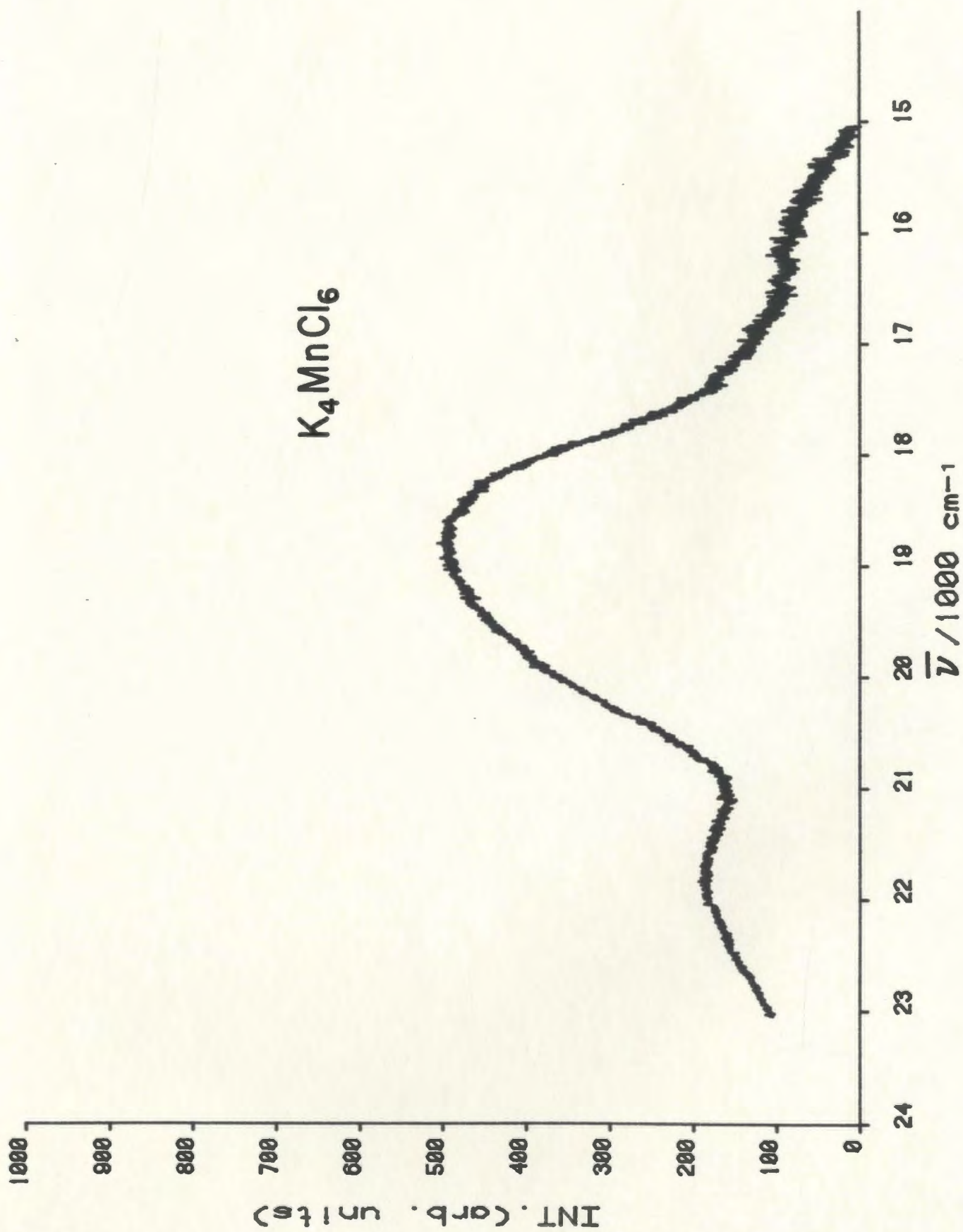


Figure 101. Visible spectrum of  $\text{K}_3\text{Mn}_2\text{Cl}_7$  at room temperature.



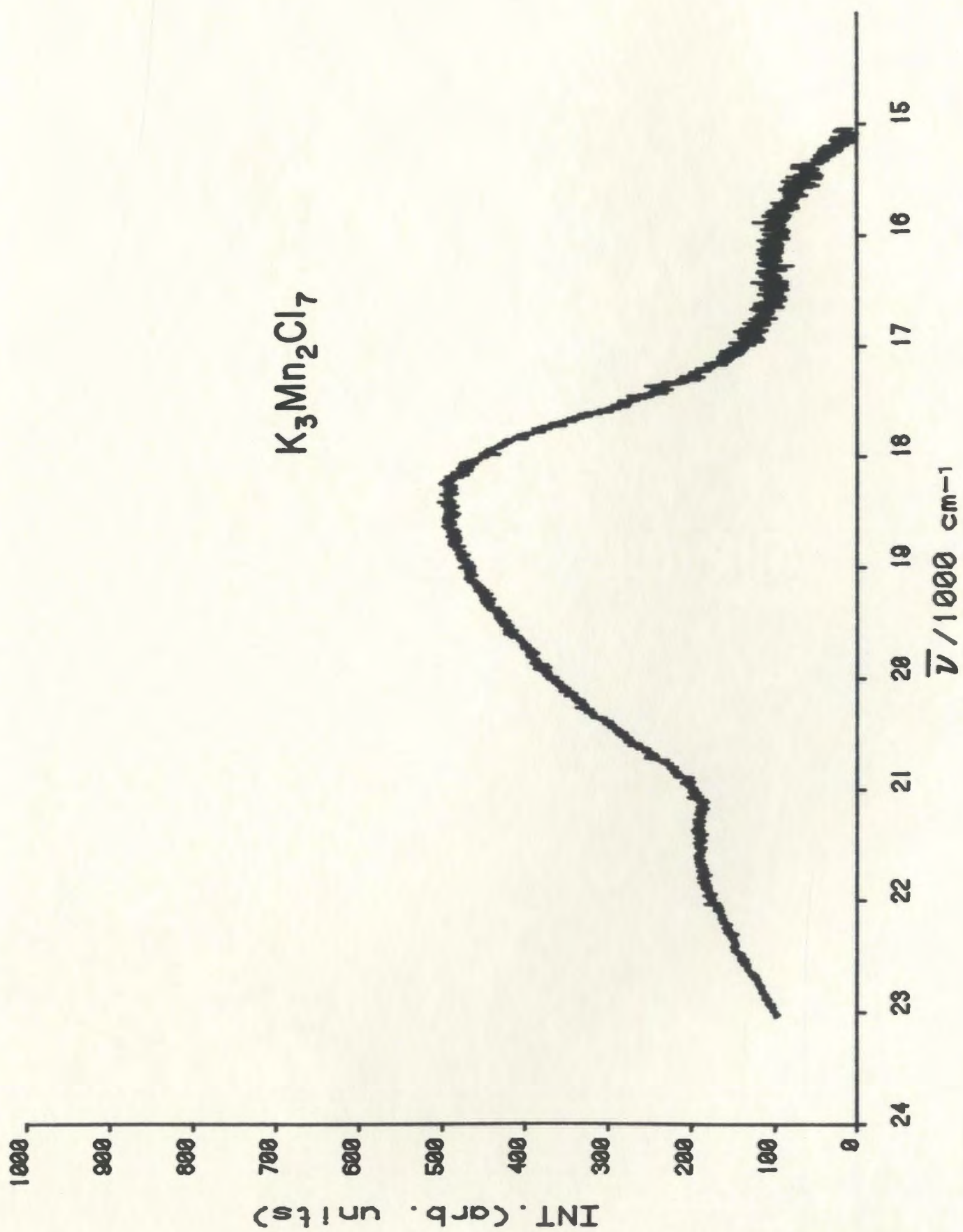


Table 37. Peak positions in  $\text{cm}^{-1}$  and assignments for solid  $\text{KMnCl}_3$ ,  $\text{K}_4\text{MnCl}_6$  and  $\text{K}_3\text{Mn}_2\text{Cl}_7$  at room temperature.

Assignments	$\text{KMnCl}_3$	$\text{KMnCl}_3^{92}$	$\text{K}_4\text{MnCl}_6$	$\text{K}_4\text{MnCl}_6^{92}$	$\text{K}_3\text{Mn}_2\text{Cl}_7$
${}^6\text{A}_{1g}({}^6\text{S}) \rightarrow {}^4\text{T}_{1g}({}^4\text{G})$	18729	19700	18885	19460	18709
$\rightarrow {}^4\text{T}_{2g}({}^4\text{G})$	21788	22960	21788	22900	21788

Figure 102. Visible spectrum of  $\text{NaMnCl}_3$  at room temperature.



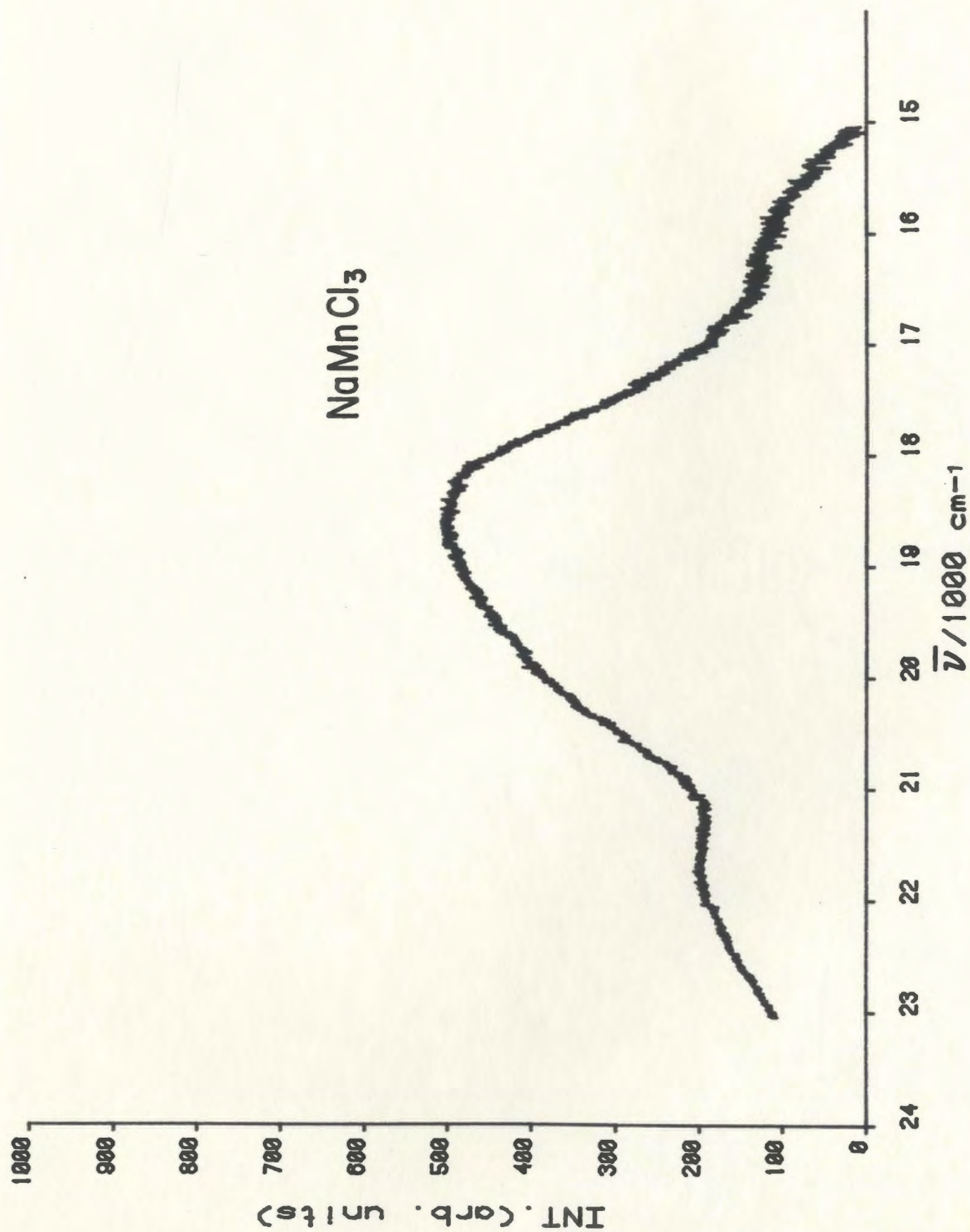


Figure 103. Visible spectrum of  $\text{Na}_2\text{MnCl}_4$  at room temperature.

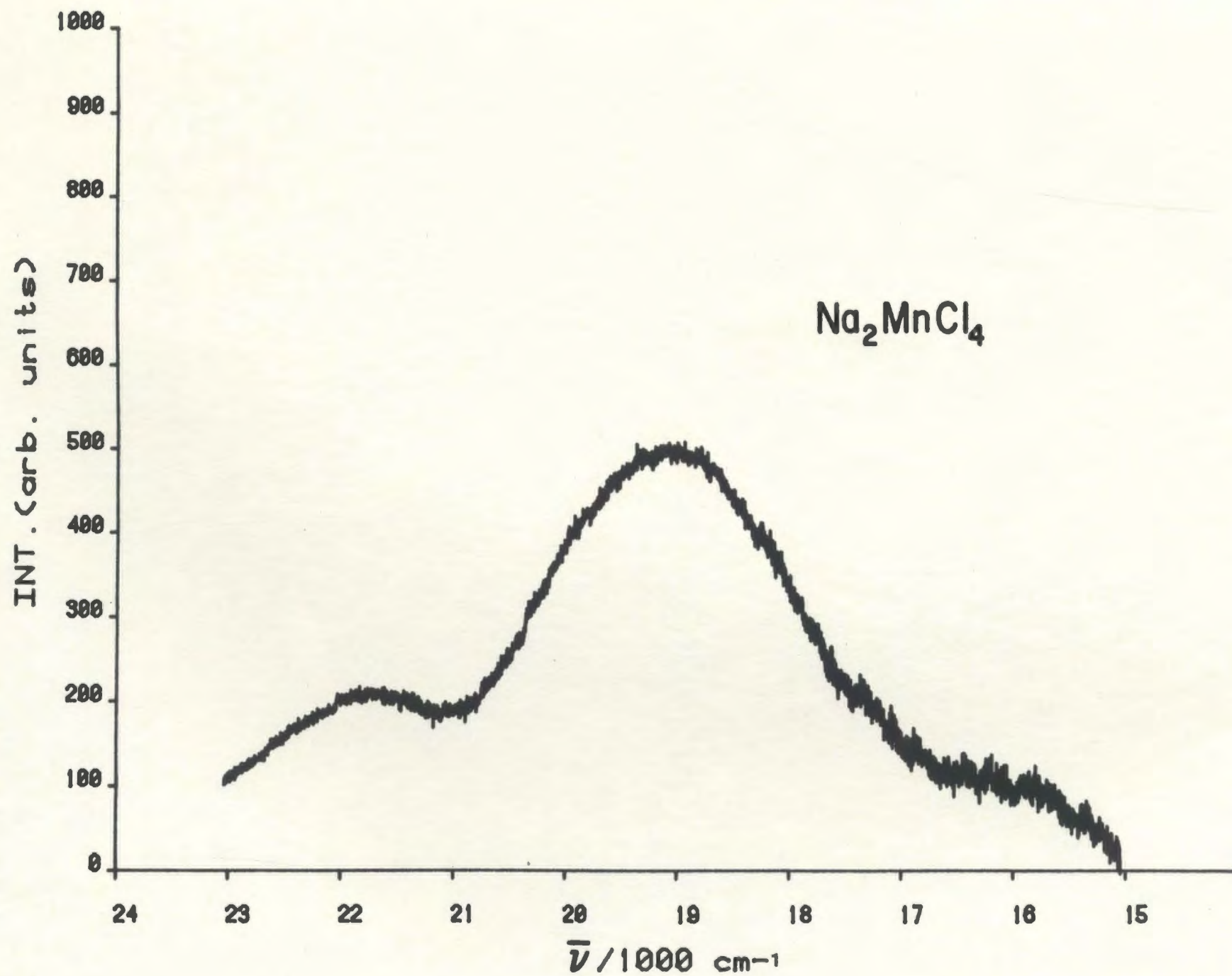




Figure 104. Visible spectrum of  $\text{Na}_6\text{MnCl}_8$  at room temperature.

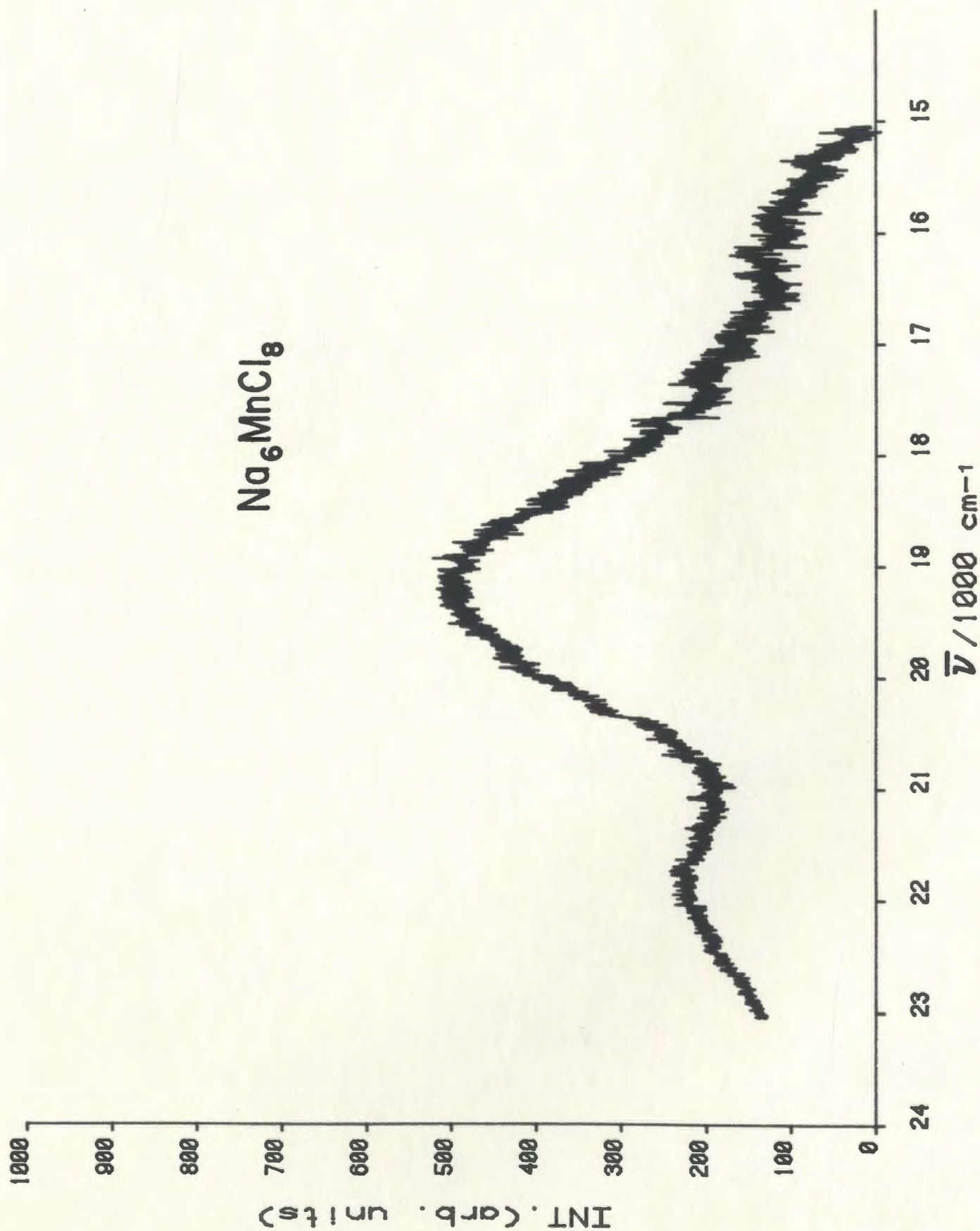


Table 38. Assignments and peak positions in  $\text{cm}^{-1}$  for solid  $\text{NaMnCl}_3$ ,  $\text{Na}_2\text{MnCl}_4$  and  $\text{Na}_6\text{MnCl}_8$  at room temperature.

Assignments	$\text{NaMnCl}_3$	$\text{Na}_2\text{MnCl}_4$	$\text{Na}_6\text{MnCl}_8$	Suzuki phase <sup>96</sup>
${}^6\text{A}_{1g}({}^6\text{S}) \rightarrow {}^4\text{T}_{1g}({}^4\text{G})$	18786	19042	19256	19242
$\rightarrow {}^4\text{T}_{2g}({}^4\text{G})$	21788	21788	21788	22878



#### 4.4.2 Molten State

(i)  $\text{Cs}_2\text{MnCl}_4$ ,  $\text{Cs}_3\text{MnCl}_5$ ,  $\text{K}_4\text{MnCl}_6$  and  $\text{Na}_6\text{MnCl}_8$

The visible spectra of  $\text{Cs}_2\text{MnCl}_4$ ,  $\text{Cs}_3\text{MnCl}_5$ ,  $\text{K}_4\text{MnCl}_6$  and  $\text{Na}_6\text{MnCl}_8$  melts are shown in figures 105, 106, 107 and 108. These compounds have yellow color in the melt and exhibit similar spectra. The peak observed at  $\sim 20142 \text{ cm}^{-1}$  in  $\text{Cs}_2\text{MnCl}_4$ ,  $\text{Cs}_3\text{MnCl}_5$  and  $\text{K}_4\text{MnCl}_6$  melts is attributed to  ${}^6\text{A}_1({}^6\text{S}) \rightarrow {}^4\text{T}_1({}^4\text{G})$  transition. This peak is slightly shifted to lower frequency and observed at  $\sim 20042 \text{ cm}^{-1}$  in  $\text{Na}_6\text{MnCl}_8$  melt. This peak was observed in the spectra of melt  $\text{MnCl}_2\text{-CsCl}$  mixtures<sup>23</sup> at  $\approx 20000 \text{ cm}^{-1}$ . The peak observed at  $\sim 15892 \text{ cm}^{-1}$  in the melts is most probably due to Manganese oxide<sup>99,100</sup> impurity in the samples. Since there is no peak reported below  $19000 \text{ cm}^{-1}$  in the optical spectra of  $\text{MnCl}_2\text{-CsCl}$  melts<sup>23</sup>,  $[\text{MnX}_4]^{2-}$  melts<sup>90</sup>,  $[\text{MnCl}_4]^{2-}$  melt<sup>88,89</sup>, and  $[\text{MnX}_4]^{2-}$  solutions<sup>86</sup>, then the peak observed at  $\sim 17392 \text{ cm}^{-1}$  in  $\text{Cs}_2\text{MnCl}_4$ ,  $\text{Cs}_3\text{MnCl}_5$  and  $\text{K}_4\text{MnCl}_6$  melts, and the peaks observed at  $\sim 16842$ ,  $17542$  and  $18142 \text{ cm}^{-1}$  in  $\text{Na}_6\text{MnCl}_8$  melt are attributed to artifacts or to unknown impurity in the melts.

$\text{Cs}_2\text{MnCl}_4$  is isostructural with  $\text{Cs}_2\text{MgCl}_4$  which melts<sup>14</sup> with the retention of the discrete tetrahedral  $\text{MgCl}_4^{2-}$  ions. Also,  $\text{Cs}_3\text{MnCl}_5$  is isomorphous with  $\text{Cs}_3\text{MgCl}_5$  which contains<sup>17</sup> the discrete tetrahedral  $\text{MgCl}_4^{2-}$  ion in the molten state. Since Raman studies of  $\text{Cs}_2\text{MnCl}_4$  and  $\text{Cs}_3\text{MnCl}_5$  melts indicated the presence of  $\text{MnCl}_4^{2-}$  tetrahedral species, and most probably these species are present in these melts as a discrete entities because there is enough chloride to facilitate this kind of isolated species.

By comparing the spectra of  $\text{K}_4\text{MnCl}_6$  and  $\text{Na}_6\text{MnCl}_8$  melts with the spectra of  $\text{Cs}_2\text{MnCl}_4$  and  $\text{Cs}_3\text{MnCl}_5$  melts, the presence of  $\text{MnCl}_4^{2-}$  tetra-

hedral species in both melts is suggested. Band positions in  $\text{cm}^{-1}$  and assignments are shown in Table 39.

(ii)  $\text{Rb}_3\text{Mn}_2\text{Cl}_7$ ,  $\text{K}_3\text{Mn}_2\text{Cl}_7$ ,  $\text{Na}_2\text{MnCl}_4$  and  $\text{Rb}_2\text{MnCl}_4$

The visible spectra of  $\text{Rb}_3\text{Mn}_2\text{Cl}_7$ ,  $\text{K}_3\text{Mn}_2\text{Cl}_7$ ,  $\text{Na}_2\text{MnCl}_4$  and  $\text{Rb}_2\text{MnCl}_4$  melts are shown in figures 109, 110, 111 and 112. These melts have a bright yellow color. In the case of  $\text{Na}_2\text{MnCl}_4$  and  $\text{Rb}_2\text{MnCl}_4$  melts, an isolated tetrahedral  $\text{MnCl}_4^{2-}$  species is expected because there is enough chloride, but for  $\text{Rb}_3\text{Mn}_2\text{Cl}_7$  and  $\text{K}_3\text{Mn}_2\text{Cl}_7$  melts, a tetrahedral species with corner sharing is the most probable structure because the spectra and the yellow color suggest that tetrahedral coordination is retained. The peak observed at  $\sim 15892 \text{ cm}^{-1}$  in the melts is most probably due to Manganese oxide<sup>99,100</sup>. Peak positions in  $\text{cm}^{-1}$  and assignments are shown in Table 40.

(iii)  $\text{CsMnCl}_3$ ,  $\text{NaMnCl}_3$ ,  $\text{KMnCl}_3$  and  $\text{RbMnCl}_3$

The visible spectra of  $\text{CsMnCl}_3$ ,  $\text{NaMnCl}_3$ ,  $\text{KMnCl}_3$  and  $\text{RbMnCl}_3$  melts are shown in figures 113, 114, 115 and 116. These melts exhibit dark yellow color. Since these melts have yellow color, then a tetrahedral  $\text{MnCl}_4^{2-}$  species with corner sharing is expected because there is not enough chloride to form an isolated  $\text{MnCl}_4^{2-}$  entity. The peak observed at  $\sim 16000 \text{ cm}^{-1}$  in the melts is due to Manganese oxide<sup>99,100</sup>. Band positions and assignments are shown in Table 41.

(iv)  $\text{MnCl}_2$ ,  $\text{CsMn}_4\text{Cl}_9$ ,  $\text{NaMn}_4\text{Cl}_9$  and  $\text{Na}_2\text{Mn}_3\text{Cl}_8$

The visible spectra of  $\text{MnCl}_2$ ,  $\text{CsMn}_4\text{Cl}_9$ ,  $\text{NaMn}_4\text{Cl}_9$  and  $\text{Na}_2\text{Mn}_3\text{Cl}_8$  melts are shown in figures 117, 118, 119 and 120.  $\text{MnCl}_2$ ,  $\text{CsMn}_4\text{Cl}_9$  and  $\text{NaMn}_4\text{Cl}_9$



Figure 105. Visible spectrum of molten  $\text{Cs}_2\text{MnCl}_4$  at 906 K.



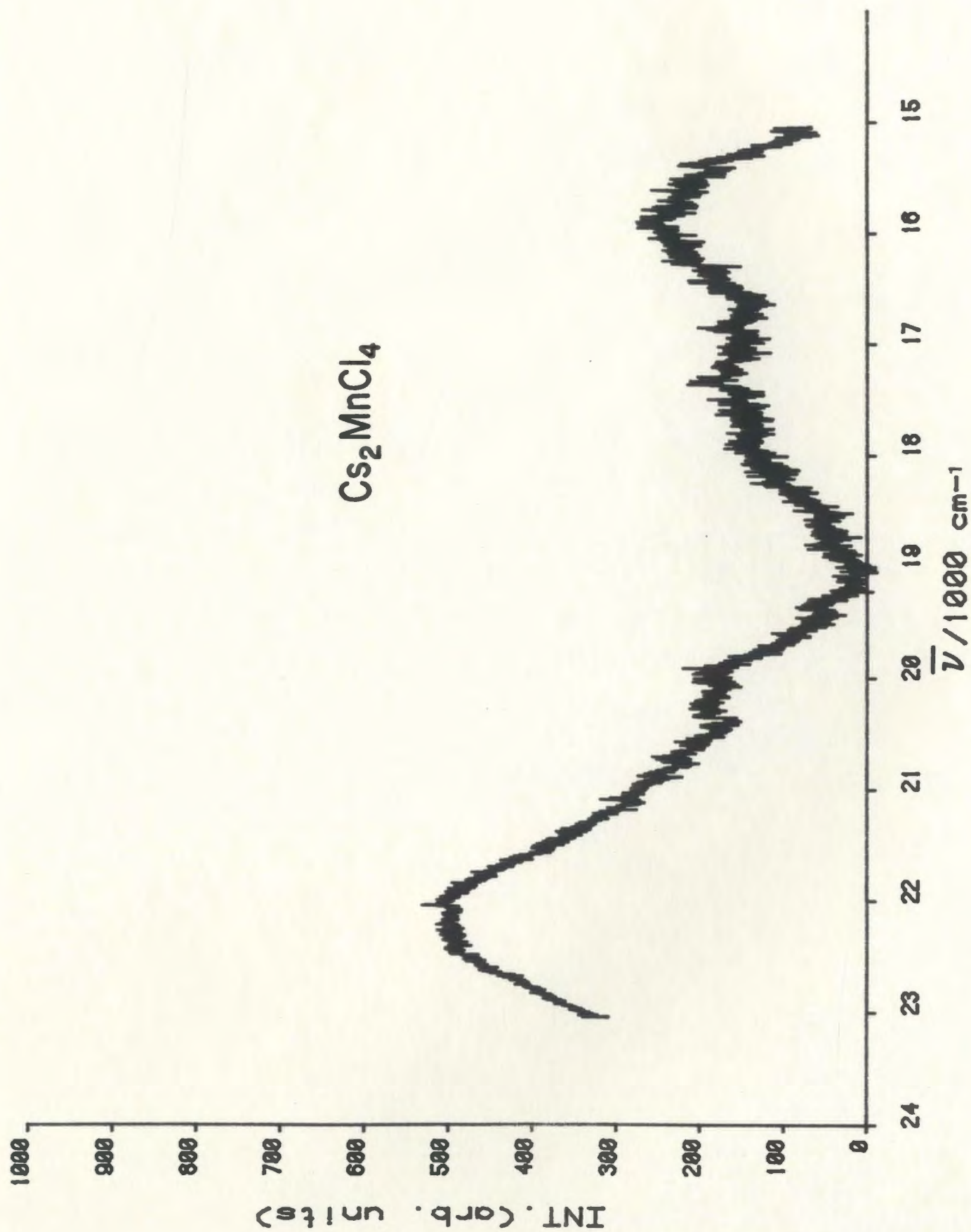


Figure 106. Visible spectrum of molten  $\text{Cs}_3\text{MnCl}_5$  at 906 K.

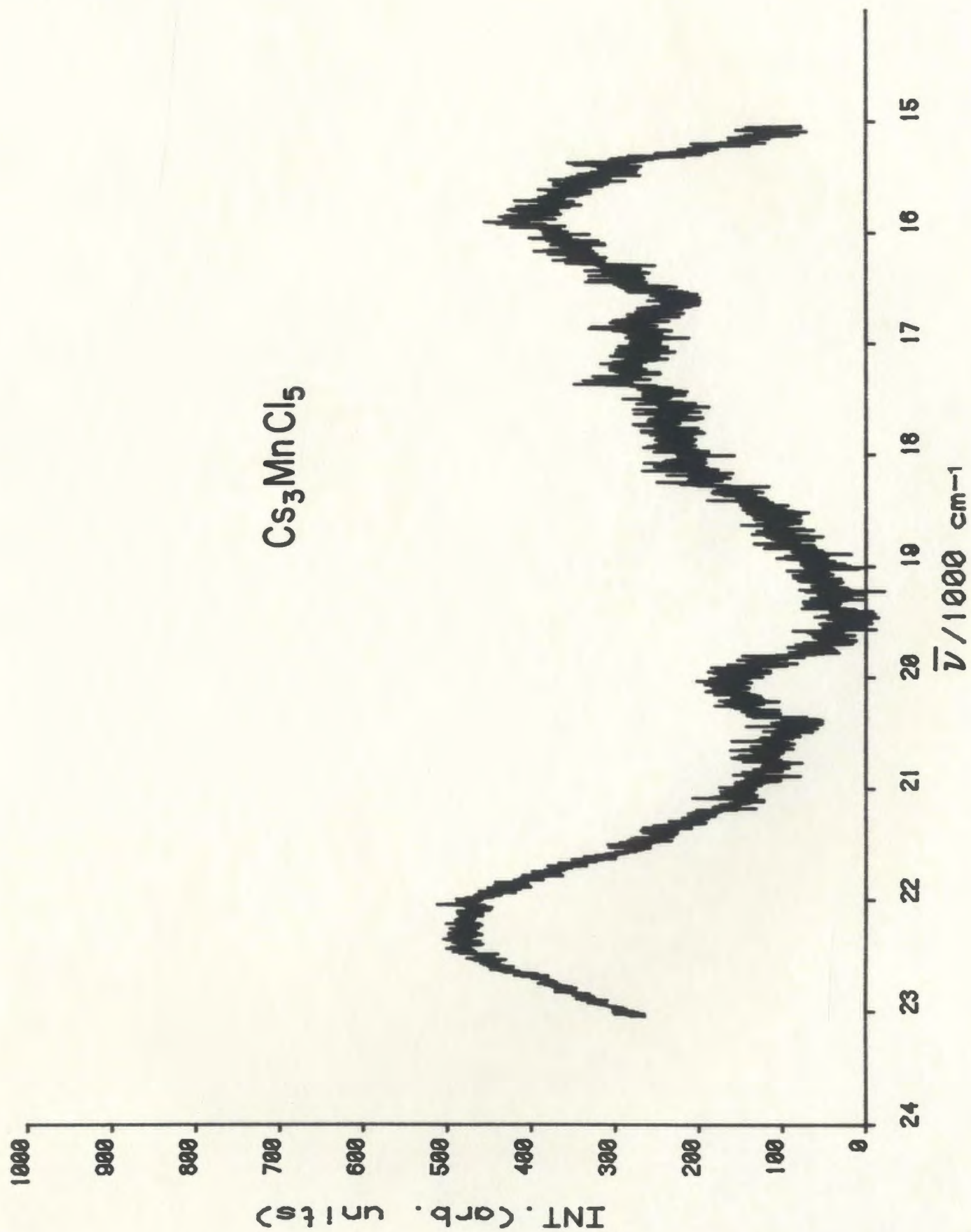




Figure 107. Visible spectrum of molten  $\text{K}_4\text{MnCl}_6$  at 906 K.

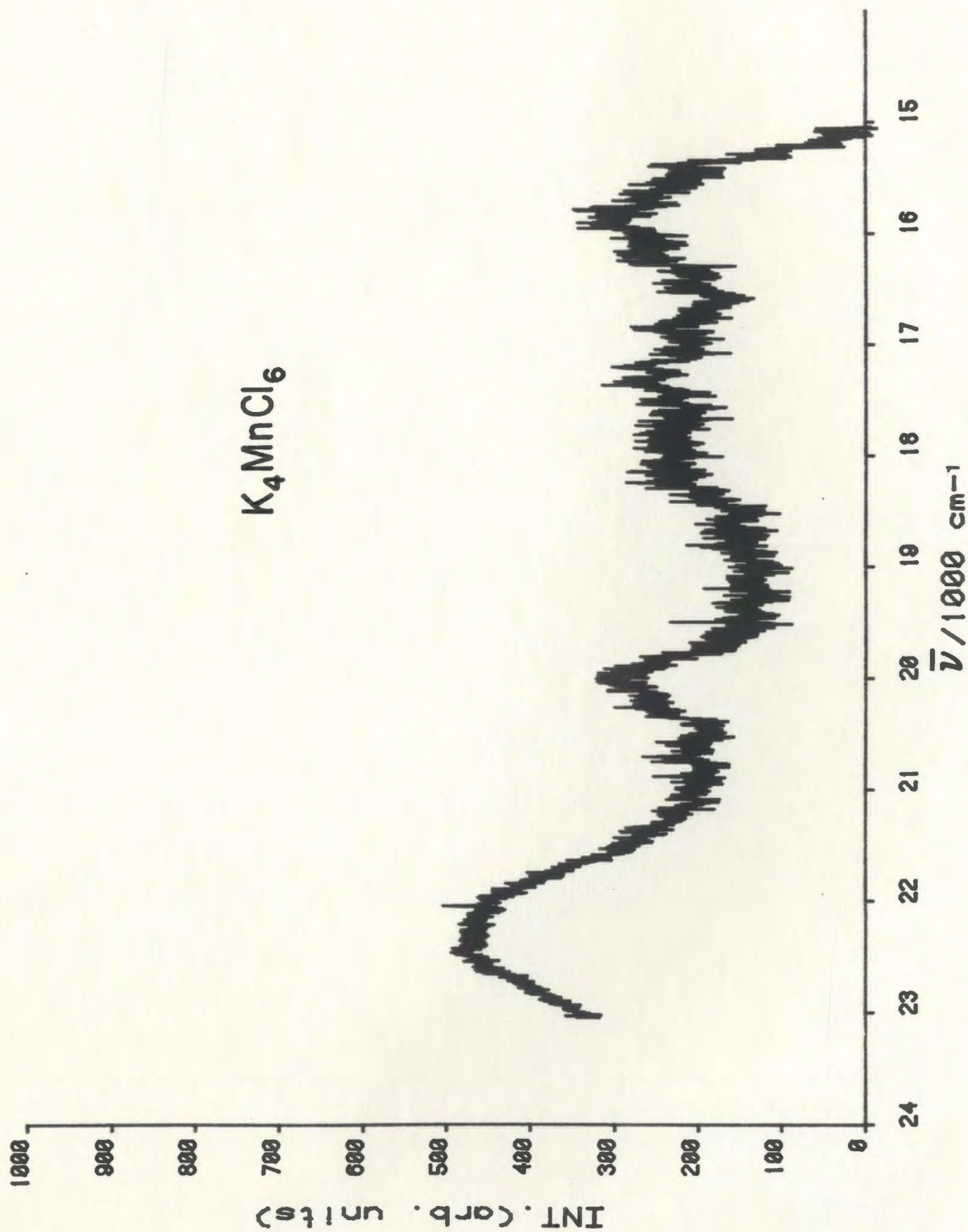
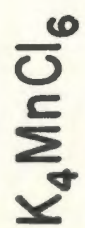


Figure 108. Visible spectrum of molten  $\text{Na}_6\text{MnCl}_8$  at 922 K.



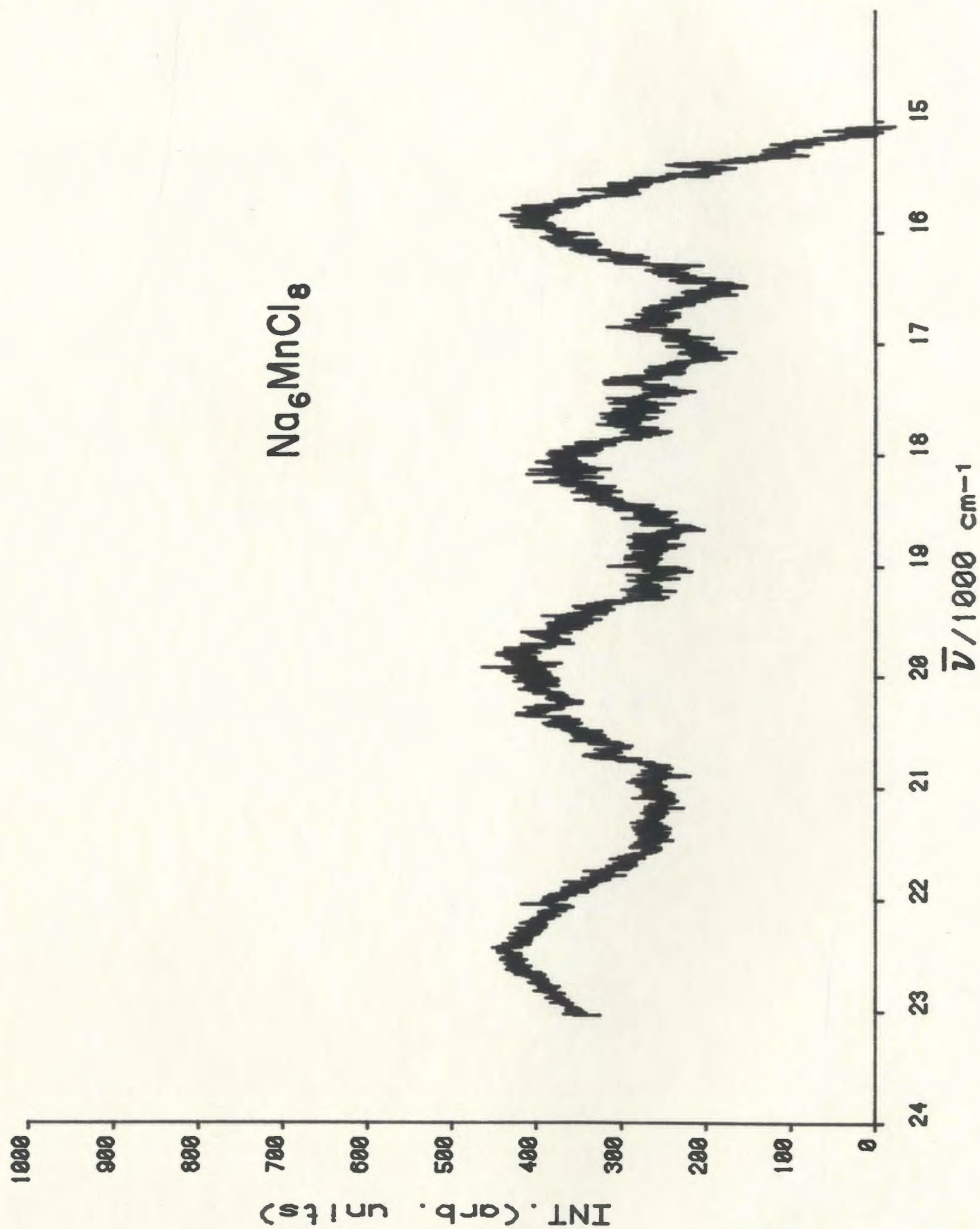
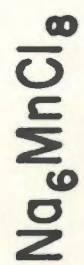


Table 39. Assignments and peak positions in  $\text{cm}^{-1}$  for  $\text{Cs}_2\text{MnCl}_4$ ,  $\text{Cs}_3\text{MnCl}_5$ ,  $\text{K}_4\text{MnCl}_6$ ,  $\text{Na}_6\text{MnCl}_8$  and  $\text{MnCl}_2\text{-CsCl}$  melts.

Assignments	$\text{Cs}_2\text{MnCl}_4$	$\text{Cs}_3\text{MnCl}_5$	$\text{K}_4\text{MnCl}_6$	$\text{Na}_6\text{MnCl}_8$	$\text{MnCl}_2\text{-CsCl}^{23}$ (0.33-0.67)
${}^6\text{A}_1({}^6\text{S}) \rightarrow {}^4\text{T}_1({}^4\text{G})$	20142	20142	20142	20042	20000
$\rightarrow {}^4\text{T}_2({}^4\text{G})$	22292	22292	22292	22492	22750

Figure 109. Visible spectrum of molten  $\text{Rb}_3\text{Mn}_2\text{Cl}_7$  at  
900 K.



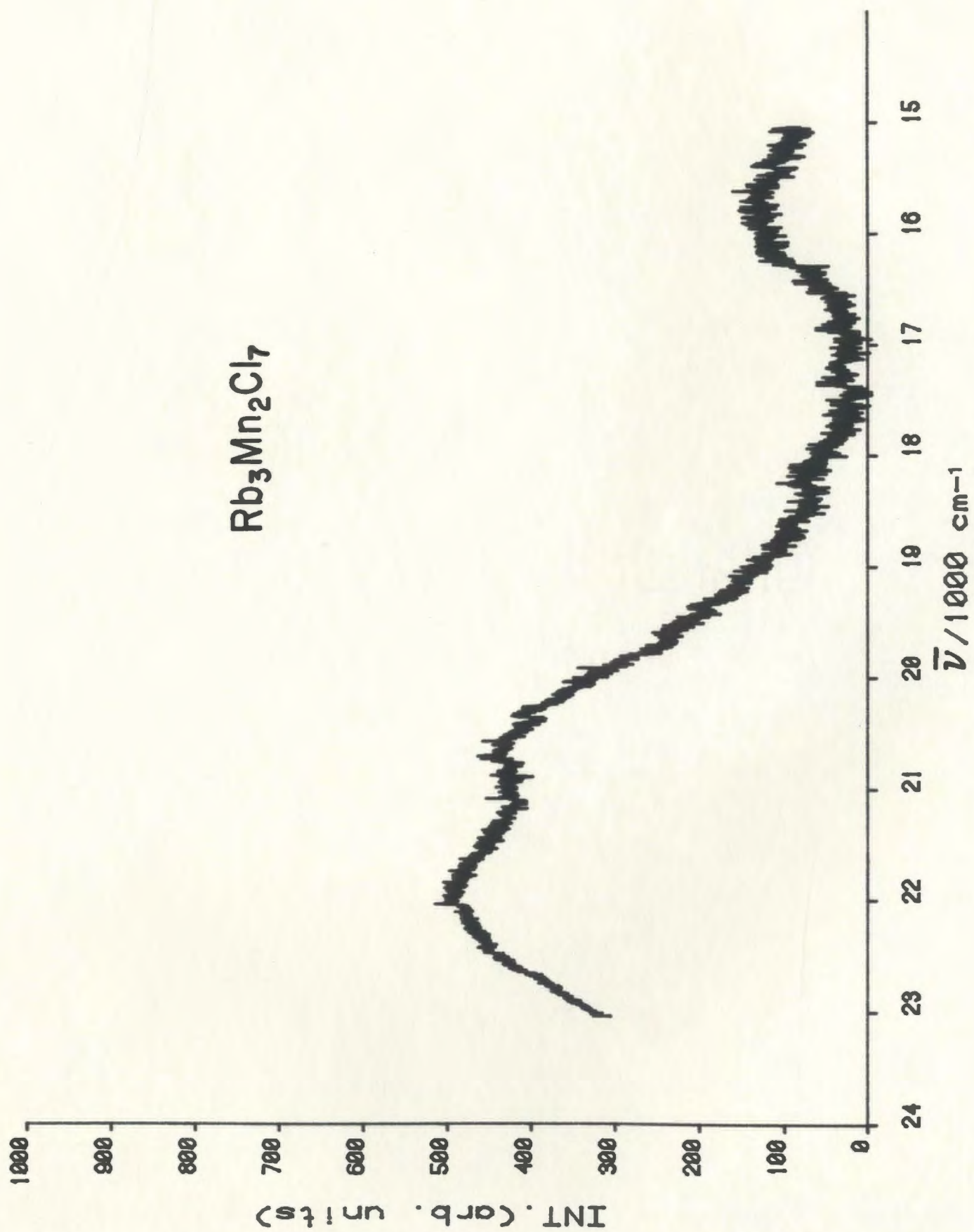
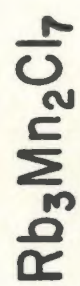


Figure 110. Visible spectrum of molten  $\text{K}_3\text{Mn}_2\text{Cl}_7$  at  
900 K.

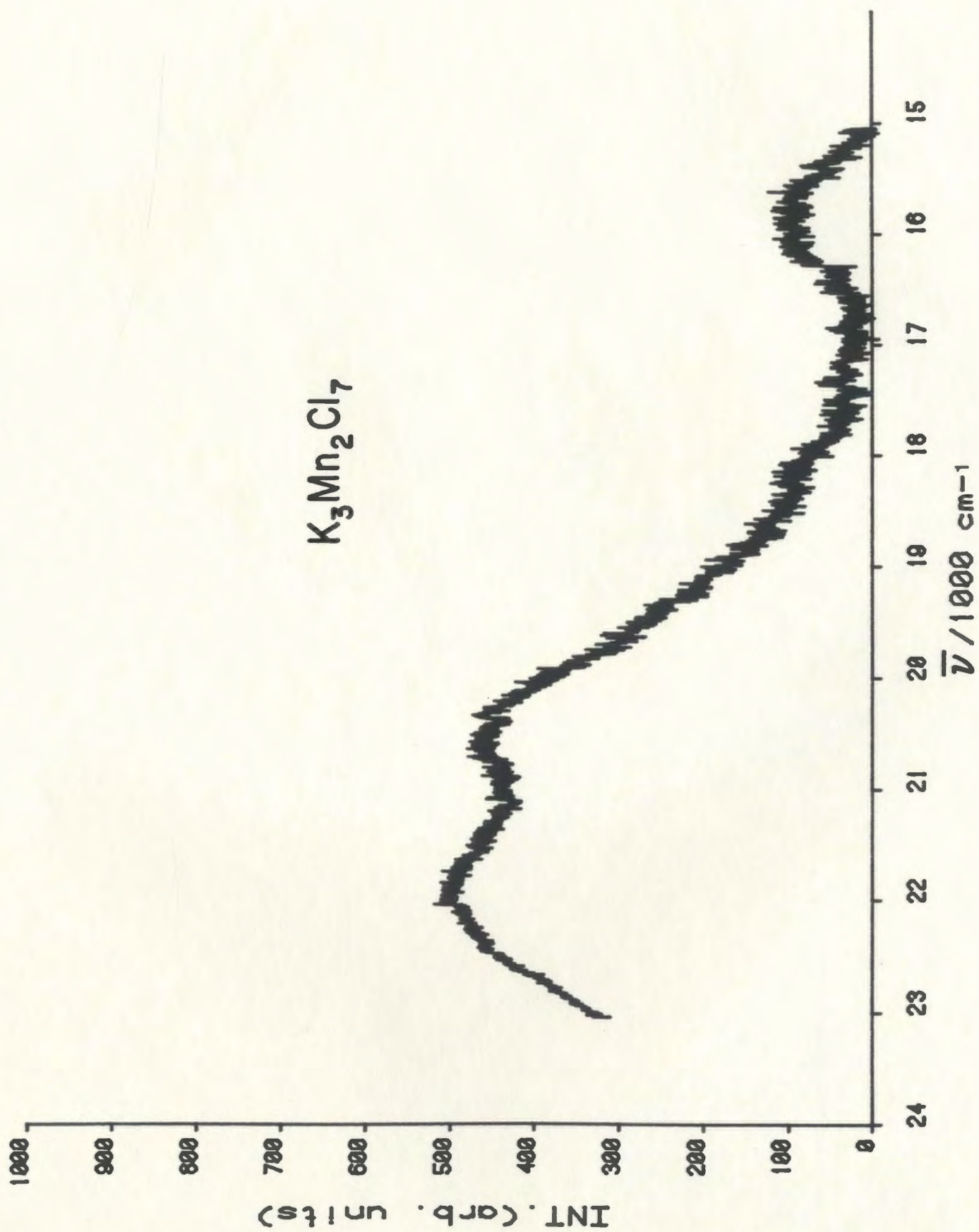




Figure 111. Visible spectrum of molten  $\text{Na}_2\text{MnCl}_4$  at  
900 K.

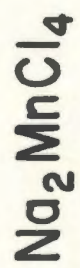


Figure 112. Visible spectrum of molten  $\text{Rb}_2\text{MnCl}_4$  at 915 K.



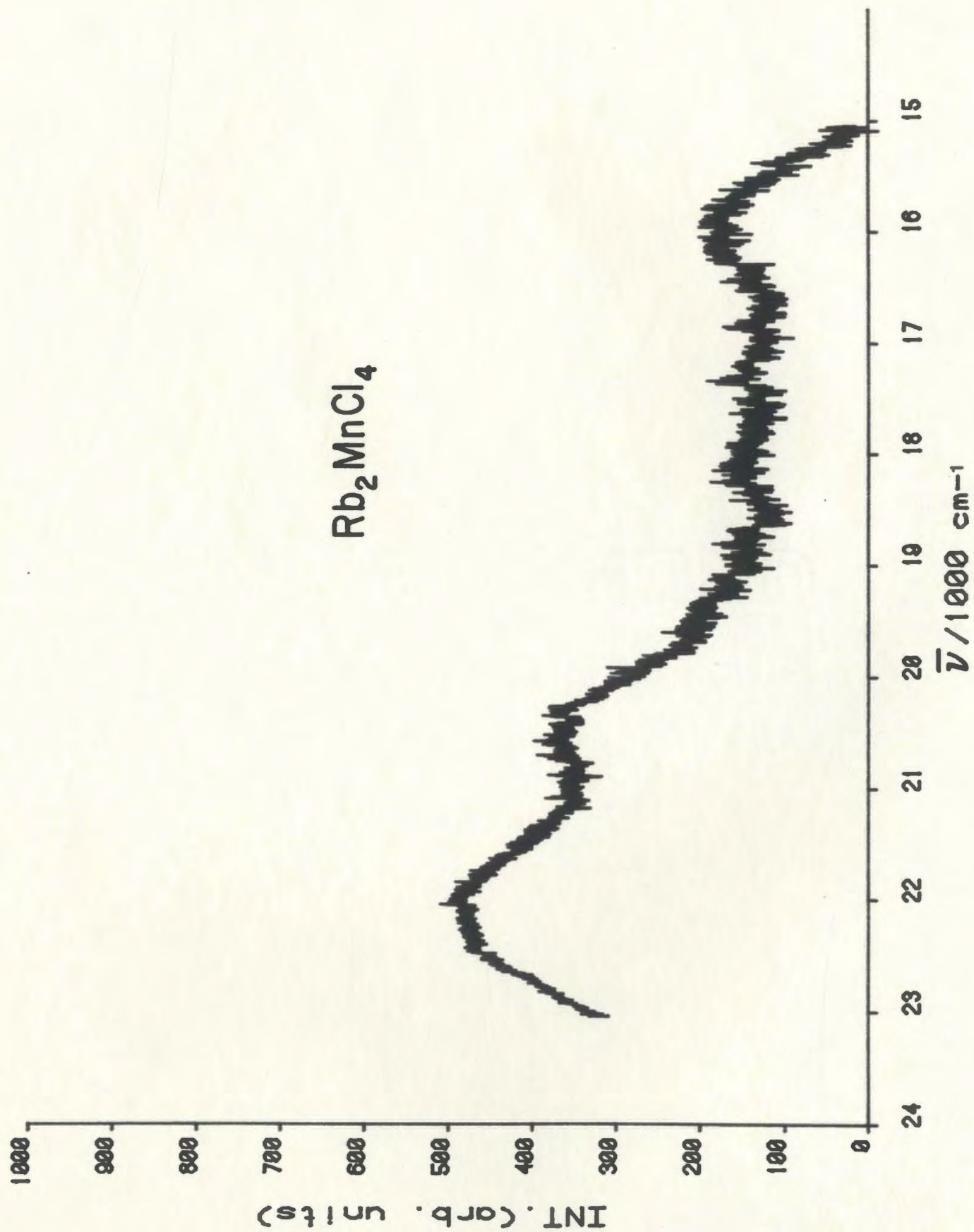


Table 40. Peak positions in  $\text{cm}^{-1}$  and assignments for  $\text{Rb}_3\text{Mn}_2\text{Cl}_7$ ,  $\text{K}_3\text{Mn}_2\text{Cl}_7$ ,  $\text{Na}_2\text{MnCl}_4$ ,  $\text{Rb}_2\text{MnCl}_4$  melts and  $[\text{MnCl}_4]^{2-}$  solution<sup>86</sup>.

Assignments	$\text{Rb}_3\text{Mn}_2\text{Cl}_7$	$\text{K}_3\text{Mn}_2\text{Cl}_7$	$\text{Na}_2\text{MnCl}_4$	$\text{Rb}_2\text{MnCl}_4$	$[\text{MnCl}_4]^{2-}$ <sup>86</sup>
${}^6\text{A}_1({}^6\text{S}) \rightarrow {}^4\text{T}_1({}^4\text{G})$	20692	20692	20692	20692	21300
$\rightarrow {}^4\text{T}_2({}^4\text{G})$	22062	22062	22292	22292	22530

Figure 113. Visible spectrum of molten  $\text{CsMnCl}_3$  at  
906 K.



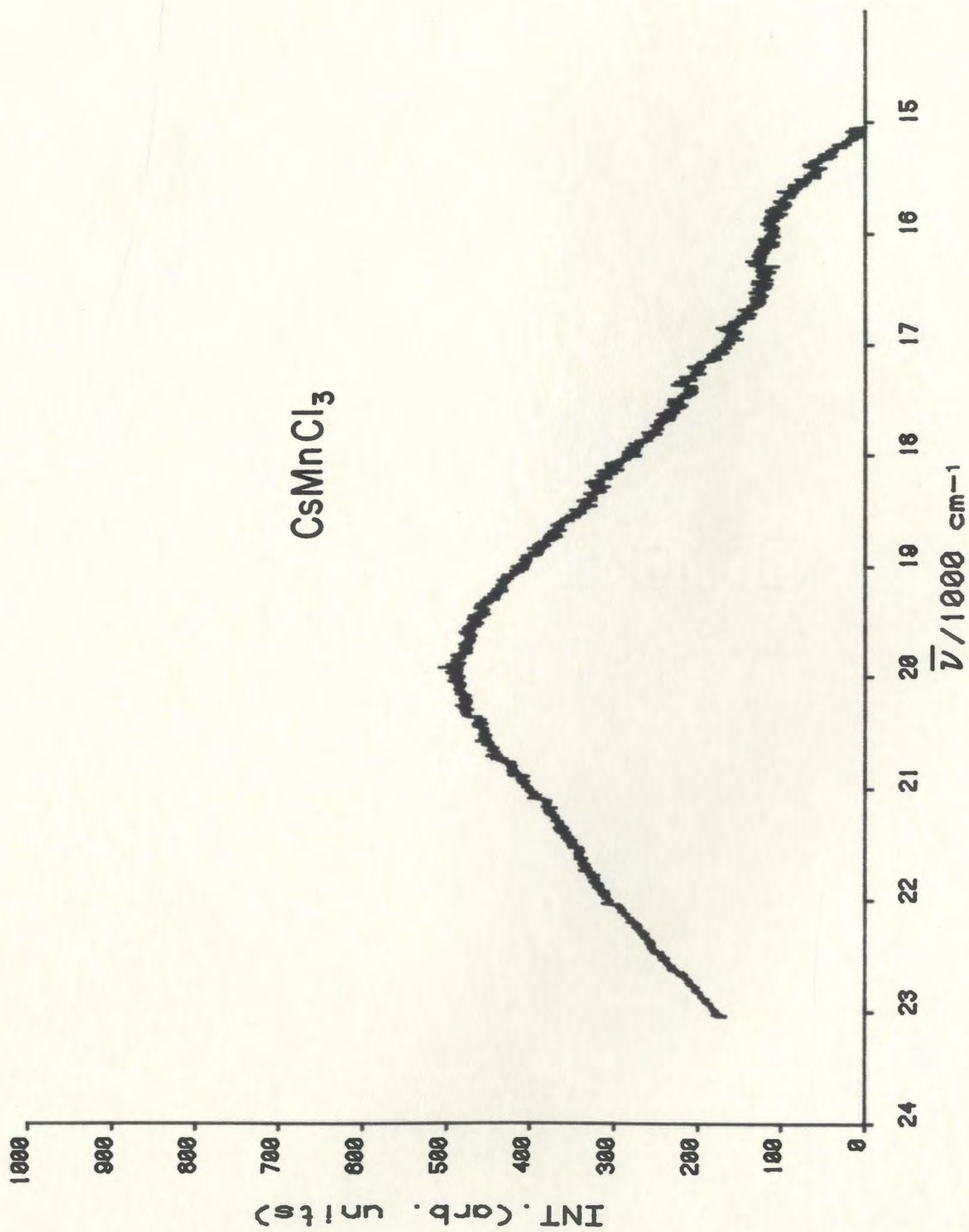


Figure 114. Visible spectrum of molten  $\text{NaMnCl}_3$  at  
900 K.

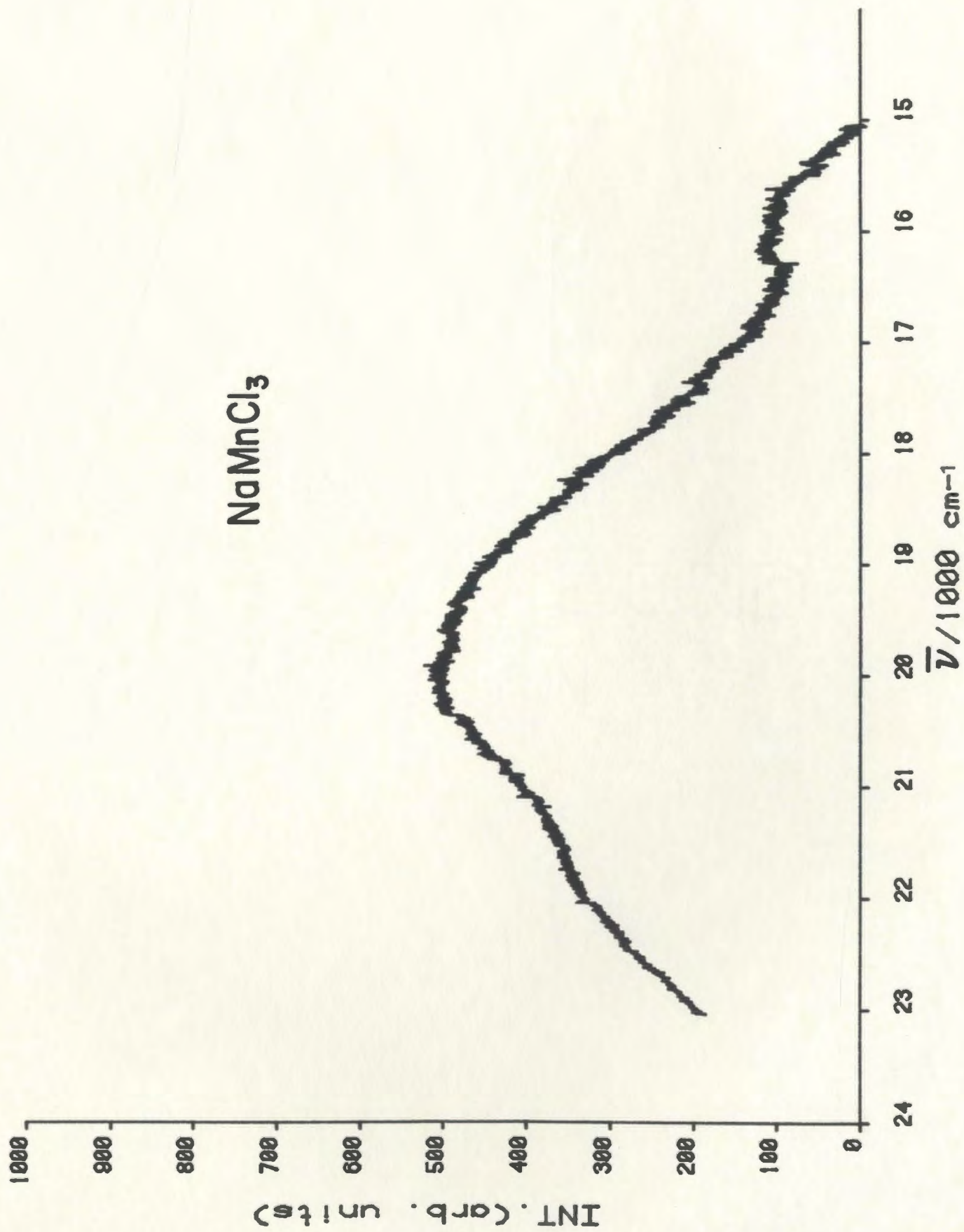




Figure 115. Visible spectrum of molten  $\text{KMnCl}_3$  at 906 K.

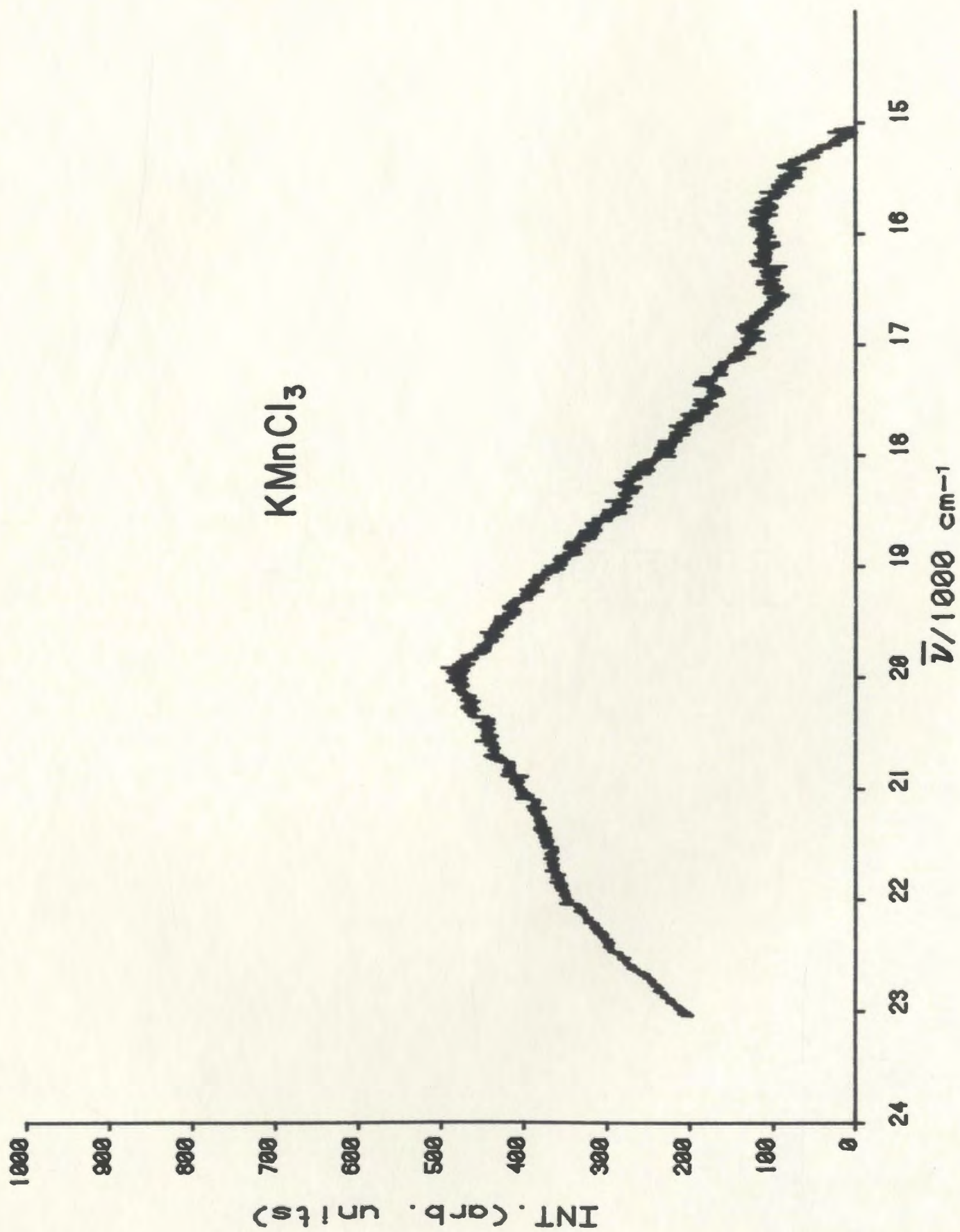


Figure 116. Visible spectrum of molten  $\text{RbMnCl}_3$  at 906 K.



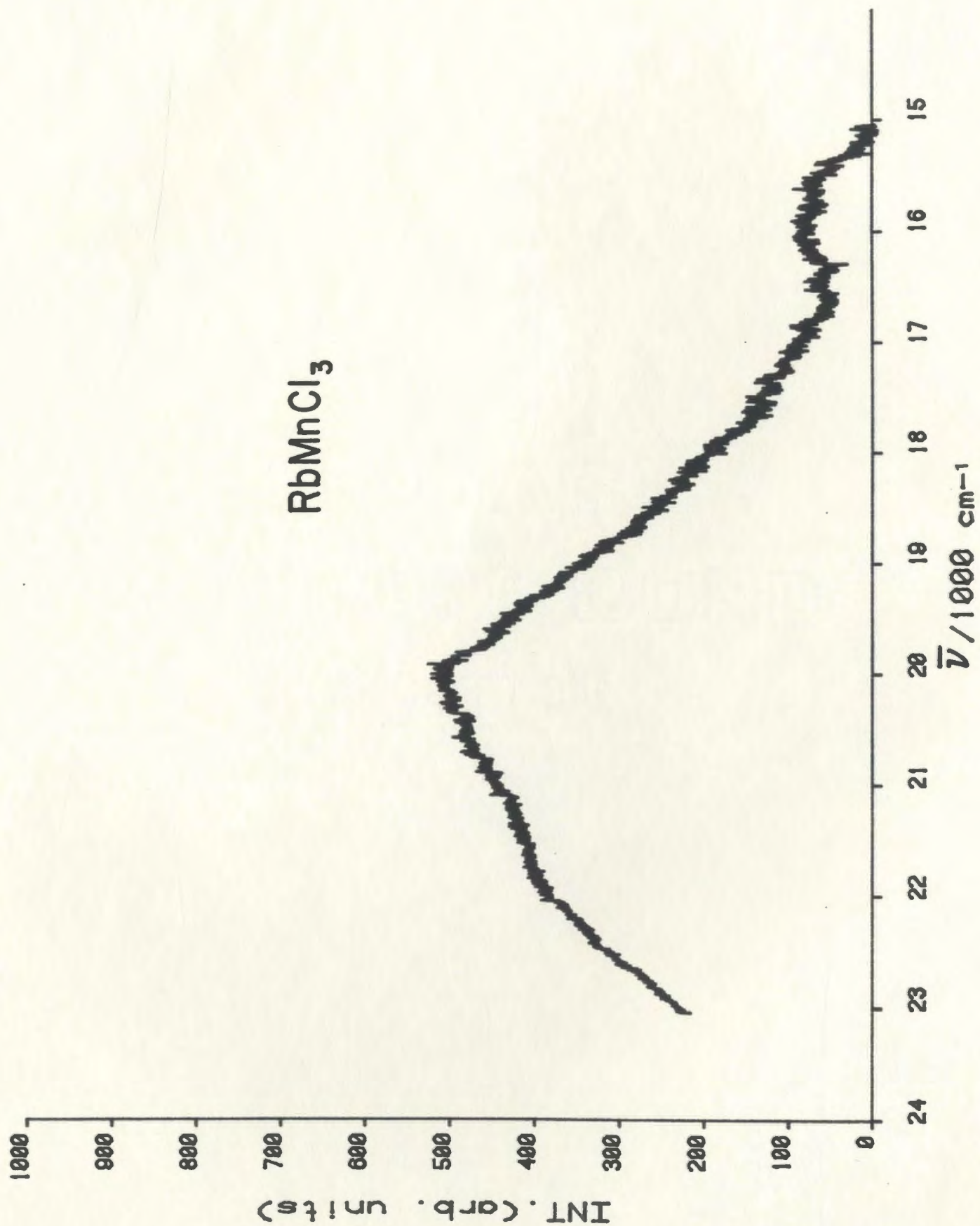
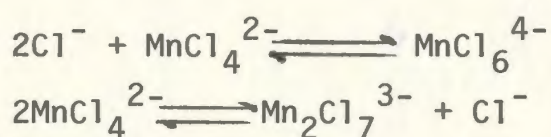


Table 41. Assignments and peak positions in  $\text{cm}^{-1}$  for  $\text{CsMnCl}_3$ ,  $\text{NaMnCl}_3$ ,  $\text{KMnCl}_3$ ,  $\text{RbMnCl}_3$  and  $\text{MnCl}_2\text{-CsCl}$  melts.

Assignments	$\text{CsMnCl}_3$	$\text{NaMnCl}_3$	$\text{KMnCl}_3$	$\text{RbMnCl}_3$	$\text{MnCl}_2\text{-CsCl}^{23}$ (0.5:0.5)
${}^6\text{A}_1({}^6\text{S}) \rightarrow {}^4\text{T}_1({}^4\text{G})$	19942	19942	19975	19975	20000
$\rightarrow {}^4\text{T}_2({}^4\text{G})$	21739	21739	21739	21739	23050

melts have orange-slightly red color, while  $\text{Na}_2\text{Mn}_3\text{Cl}_8$  melt exhibit a yellow-orange color. The slight red color and the band positions in the visible spectra for melts of high  $\text{MnCl}_2$  content suggest the presence of a small amount of octahedrally coordinated  $\text{Mn}^{2+}$ . The results suggest that Mn remains mostly tetrahedral coordination but octahedral coordination may be present. However Raman studies indicated that the coordination of Mn is ill-defined due to rapid exchange of ligands:



The formation of these ions take place through corners sharing. The peak observed at  $\sim 16000 \text{ cm}^{-1}$  in  $\text{NaMn}_4\text{Cl}_9$  and  $\text{Na}_2\text{Mn}_3\text{Cl}_8$  melts is attributed to Manganese oxide<sup>99,100</sup>. Band positions in  $\text{cm}^{-1}$  and assignments are shown in Table 42.

It was possible to differentiate between the compounds which have tetrahedral manganese from the ones in which the manganese is octahedrally coordinated by chlorine atoms on the basis of their visible spectra. In the molten state, the tetrahedral  $\text{MnCl}_4^{2-}$  species as an isolated entities or through corners sharing are the predominant species in the melts.



Figure 117. Visible spectrum of molten  $\text{MnCl}_2$  at 974 K.

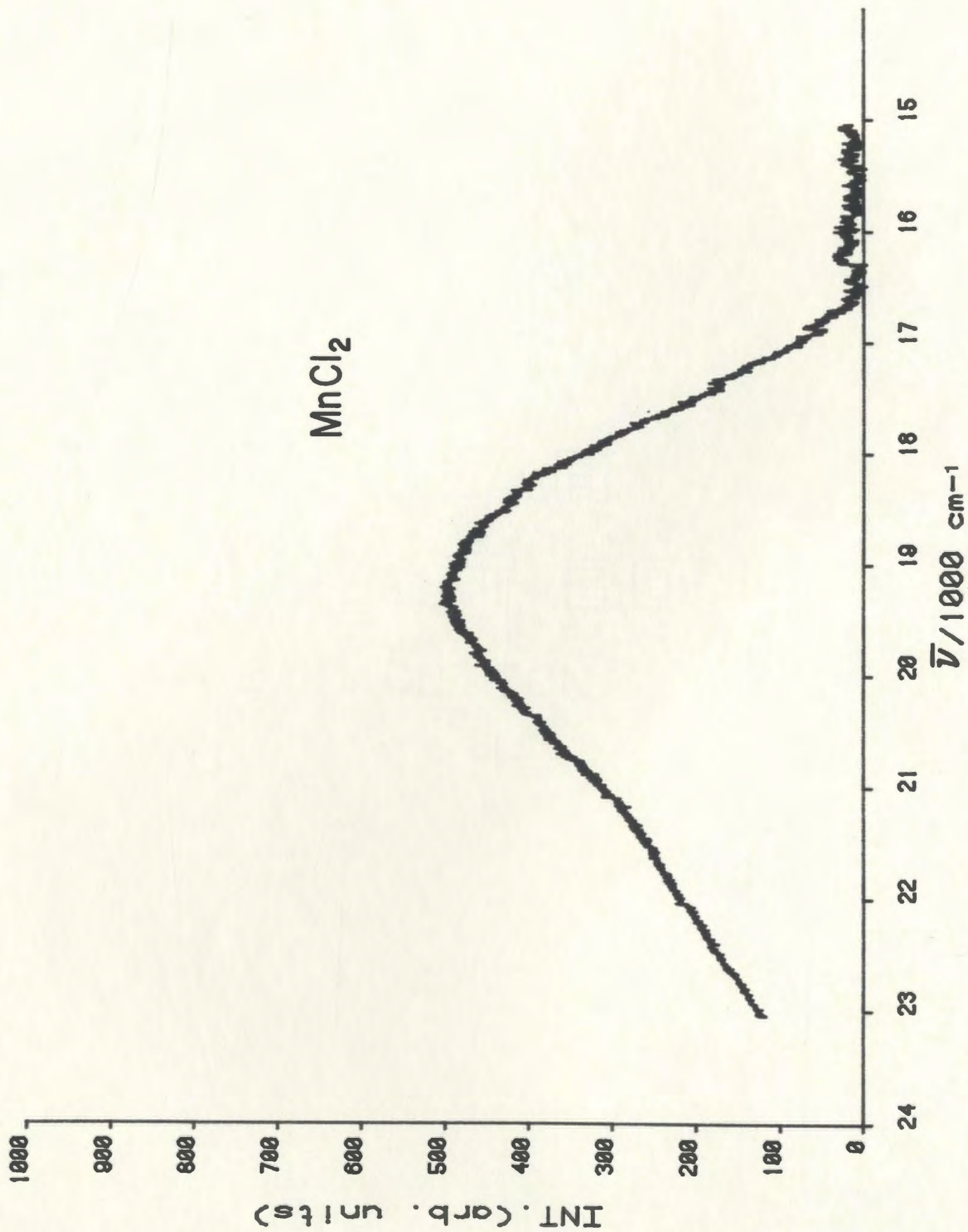


Figure 118. Visible spectrum of molten  $\text{CsMn}_4\text{Cl}_9$  at  
925 K.



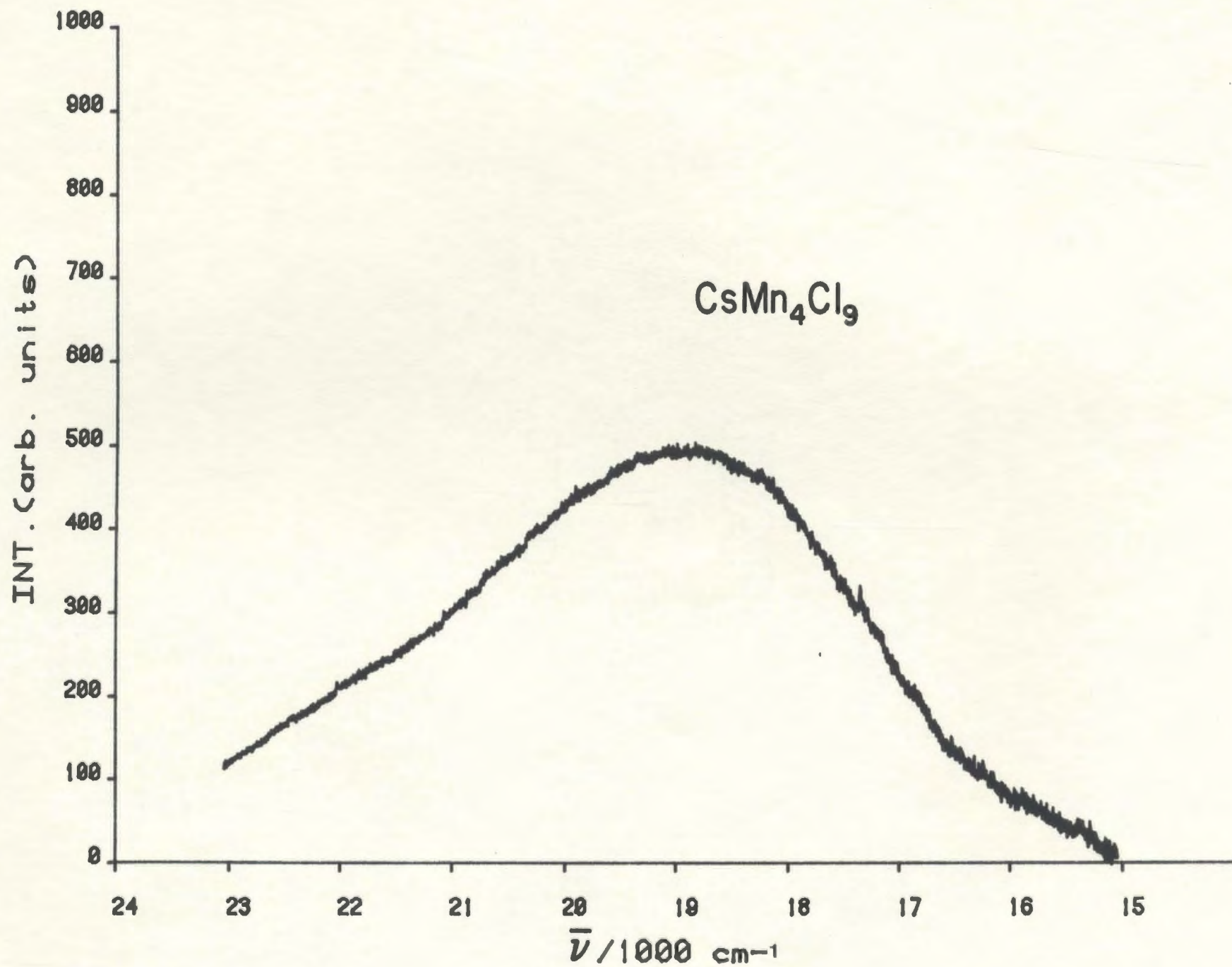


Figure 119. Visible spectrum of molten  $\text{NaMn}_4\text{Cl}_9$  at 916 K.

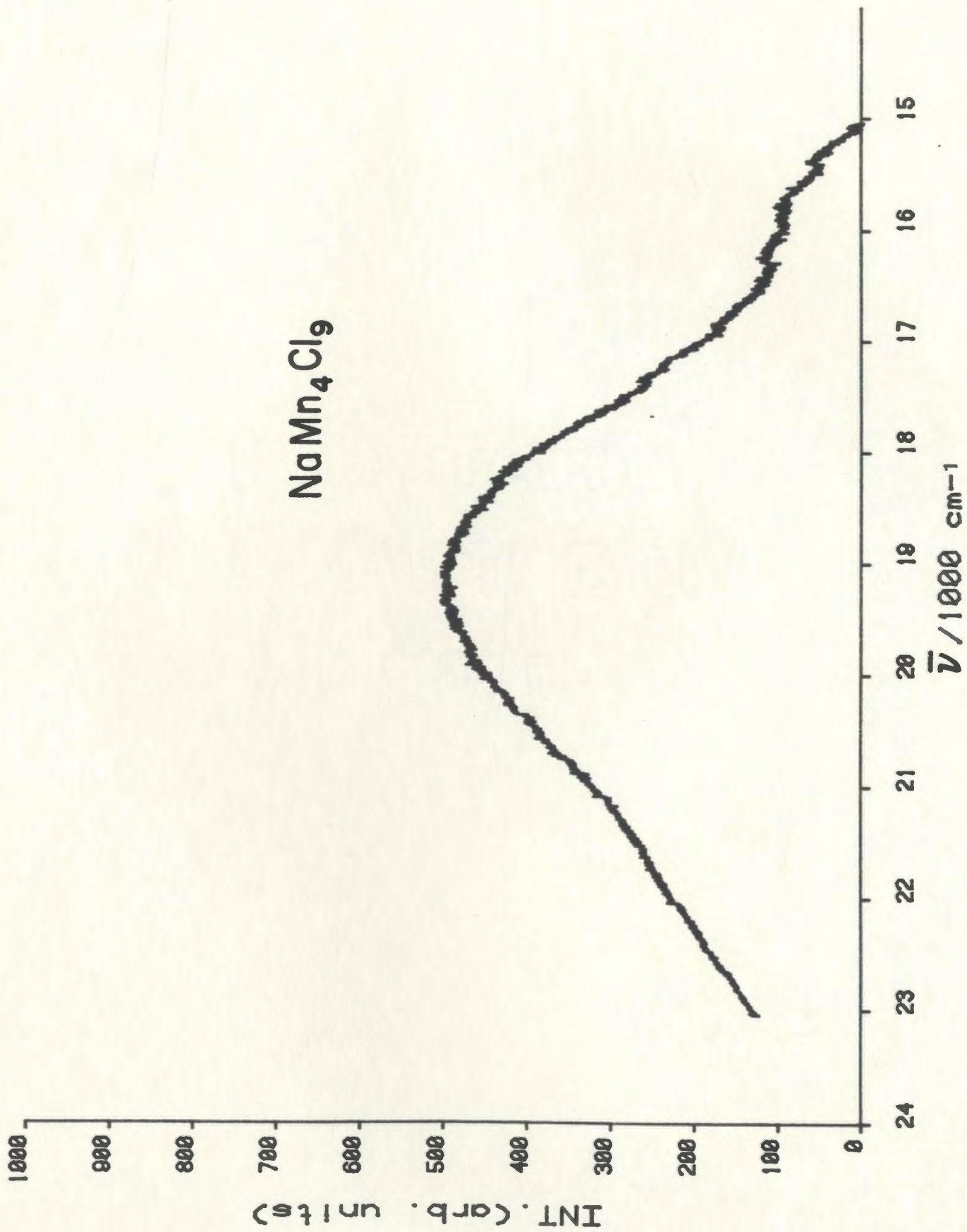




Figure 120. Visible spectrum of molten  $\text{Na}_2\text{Mn}_3\text{Cl}_8$  at 901 K.

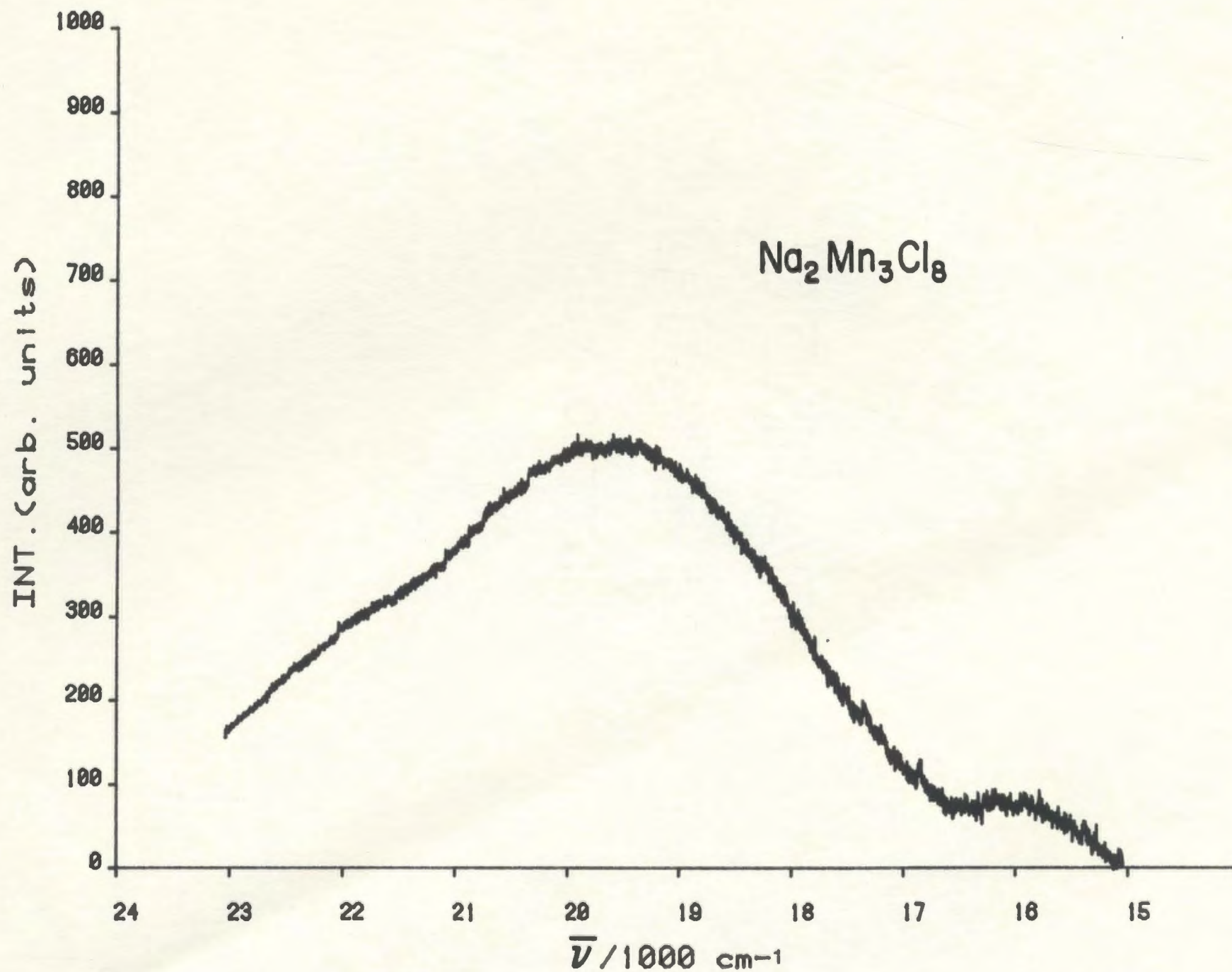


Table 42. Assignments and peak positions in  $\text{cm}^{-1}$  for  $\text{MnCl}_2$ ,  $\text{CsMn}_4\text{Cl}_9$ ,  $\text{NaMn}_4\text{Cl}_9$ ,  $\text{Na}_2\text{Mn}_3\text{Cl}_8$  and  $\text{MnCl}_2\text{-CsCl}$  melts.

Assignments	$\text{MnCl}_2$	$\text{MnCl}_2\text{-CsCl}^{23}$ (1.0:0.0)	$\text{CsMn}_4\text{Cl}_9$	$\text{MnCl}_2\text{-CsCl}^{23}$ (0.8:0.2)	$\text{NaMn}_4\text{Cl}_9$	$\text{Na}_2\text{Mn}_3\text{Cl}_8$
${}^6\text{A}_1({}^6\text{S}) \rightarrow {}^4\text{T}_1({}^4\text{G})$	19300	20000	19042	20000	19042	19542
$\rightarrow {}^4\text{T}_2({}^4\text{G})$		23300		23260		21739



## 5. Conclusion

The Raman and visible results indicate the presence of  $\text{MnCl}_4^{2-}$  ions as the predominant species for  $\text{MnCl}_2 \cdot n\text{ACl}$  melts. However for melts of high  $\text{MnCl}_2$  concentration, the Raman results suggest the presence of  $\text{MnCl}_4^{2-}$  ions as the predominant species in addition to the very short-lived species such as,  $\text{Mn}_2\text{Cl}_7^{3-}$ . The visible results for the melts suggest the presence of a small fraction of  $\text{MnCl}_6^{4-}$  ions in addition to the predominant  $\text{MnCl}_4^{2-}$  ions.

The Raman results for  $\text{MgCl}_2 \cdot n\text{ACl}$  melts indicate the presence of equilibrium concentrations of  $\text{MgCl}_4^{2-}$  and  $\text{Mg}_2\text{Cl}_7^{3-}$  ions as the predominant species in melts of moderate  $\text{MgCl}_2$  content. A third species  $\text{Mg}_2\text{Cl}_n^{4-n}$  was detected by further increment of  $\text{MgCl}_2$  concentration but the short lifetimes of the higher polymeric species makes it difficult to fully characterize their spectra.

Absorption spectra of the solid compounds in the visible range has lead to identification of tetrahedral and octahedral coordination but could not differentiate between extended array structures and discrete species. The combined visible and Raman spectra can be used to characterize the many solids formed in the  $\text{ACl-MnCl}_2$  systems.

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